ROBERT A. TAFT WATER RESEARCH CENTER

REPORT NO. TWRC-4

PB187758

OZONE TREATMENT OF SECONDARY EFFLUENTS FROM WASTEWATER TREATMENT PLANTS

ADVANCED WASTE TREATMENT RESEARCH LABORATORY - IV

Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information Springfield Va. 22151

U.S. DEPARTMENT OF THE INTERIOR
FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
OHIO BASIN REGION
Cincinnati, Ohio

42

OZONE TREATMENT OF SECONDARY EFFLUENTS FROM WASTE-WATER TREATMENT PLANTS

by

D. Th. A. Huibers, R. McNabney,
and A. Halfon

for

The Advanced Waste Treatment Research Laboratory
Robert A. Taft Water Research Center

This report is submitted in fulfillment of Contract No. 14-12-114 between the Federal Water Pollution Control Administration and the Air Reduction Company, Inc.

U. S. Department of the Interior
Federal Water Pollution Control Administration
Cincinnati, Ohio

April 9, 1969

BLANK PAGE

FOREWORD

In its assigned function as the Nation's principal natural resource agency, the United States Department of the Interior bears a special obligation to ensure that our expendable resources are conserved, that renewable resources are managed to produce optimum yields, and that all resources contribute their full measure to the progress, prosperity and security of America -- now and in the future.

This series of reports has been established to present the results of intramural and contract research carried out under the guidance of the technical staff of the FWPCA's Robert A. Taft Water Research Center for the purpose of developing new or improved wastewater treatment methods. Included is work conducted under cooperative and contractual agreements with Federal, state, and local agencies, research institutions, and industrial organizations. The reports are published essentially as submitted by the investigators. The ideas and conclusions presented are, therefore, those of the investigators and not necessarily those of the FWPCA.

Reports in this series will be distributed as supplies permit. Requests should be sent to the Office of Information, Ohio Basin Region, Federal Water Pollution Control Administration, 4676 Columbia Parkway, Cincinnati, Ohio 45226.

TABLE OF CONTENTS

	Page
Foreword	ii
Table of Contents	iii
Abstract	iv
Summary and Recommendations	v
Introduction	1
Experimental Work	3
Analytical Procedures	4
Secondary Effluent Composition	6
Ozonizer	6
Solubility and Decomposition of Ozone in Water	6
Clarification of Secondary Effluents	7
Ozonation in a Continuous Countercurrent Column	12
Equipment and Procedures	12
Results and Discussion	15
Batch Reactor Tests	22
Equipment and Procedures	22
Results and Discussion	24
Simulation of a Six-Stage Cocurrent Contacting System	37
Equipment and Procedures	37
Results and Discussion	39
Design Concepts and Criteria	44
Ozone Supply	44
Process Design	45
Plant Description	48
Capital Cost Estimate	53
Operating Costs	58
References	61

ABSTRACT

Ozone effectively lowers the chemical oxygen demand (COD) and total organic carbon (TOC) content of effluents from waste-water treatment plants. It removes odors and color from water and destroys pathogenic organisms. Residual ozone decomposes rather rapidly; it has a half life in drinking water of about 20 minutes. Tertiary treatment with ozone has the potential of an automated, trouble-free operation with low maintenance. The objectives of this research work were to devise an efficient contacting process and to make a preliminary evaluation of its economics.

Ozonation was first studied by low-shear countercurrent contacting in an 18-ft. column packed with Raschig rings. Later it was found that the rates of COD and TOC removal could be considerably increased by high-shear contacting using a turbine agitator. Kinetic data, obtained with batch reactor experiments, indicated that the optimum treatment of secondary effluent with ozone required multi-stage cocurrent contacting. A six-stage system was simulated by mixing effluent with ozone in an injector and recycling the mixture through the 18-ft. packed tower. Overall ozone-utilization efficiencies as high as 90% were obtained.

The estimated treatment cost is 7.7¢/1000 gal. to reduce the COD from 35 mg/l to 15 mg/l assuming an 80% ozone-utilization efficiency at a 10-million GPD plant. This is about equal to the estimated cost for treatment with activated carbon.

Unless the waste-water treatment plant is particularly effective, chemical clarification of the secondary effluent prior to treatment with ozone may be advantageous since that would reduce ozone consumption and result in a lower final COD and TOC.

SUMMARY AND RECOMMENDATIONS

The use of ozone for tertiary treatment of secondary effluent has proven to be economically effective. Treatment of actual effluents from the Totowa, New Jersey, and Berkeley Heights, New Jersey, trickling-filter, waste-treatment plants by ozone resulted in a product that met PHS requirements for potable water. Virtually all color, odor and turbidity were removed; and oxygen-consuming organic materials, measured as COD, were reduced to acceptable levels (below 15 mg/l). Bacteriological tests showed that no live organisms remained; and surface-active detergents, which can cause foaming, were removed. Ozone concentrations from 11 mg/l to 48 mg/l in oxygen proved equally effective.

The experimental work consisted of three main parts:

1. Ozonation in a continuous countercurrent column,
2. Batch reactor tests,
3. Simulation of six-stage cocurrent contacting.

Initially, a continuous, countercurrent, reaction system was investigated using an 18-foot glass column, 4 inches in diameter. Batch reactor tests were used to investigate the mass transfer effects on the rates of COD and TOC removal with ozone. These tests showed that the rates of COD and TOC removal were very dependent on agitation rates. This dependency results from the need for high mass-transfer rates for ozone from the gas phase to the liquid phase. The instability of ozone, coupled with low chemical-reaction rates, led to the development of a cocurrent multistage contacting system with the ozone supply, per stage, proportional to the demand as determined by the COD content. Contact between the incoming streams was effected by a high-shear injector. A comparison of the performance of this improved system with that of the countercurrent column is summarized in Table I.

Pretreatment of the secondary effluent by coagulation, sedimentation and filtration (i.e., chemical clarification) resulted in appreciable reductions of ozone usage for the particular effluents studied. The coagulant used (either lime, alum, or alum + acid) had little effect on the efficiency of clarification, but its control over effluent pH had a marked influence on the ozonation operation. In general, a low pH for the clarified effluent resulted in lower reaction rates but in higher ozone-utilization efficiencies.

TABLE I

SUMMARY OF CONTINUOUS OZONATION OF SECONDARY EFFLUENT

Effluent Origin	Reactor Type	Coagulant	O_3 Concentration in Gas Feed, mg/l	COD, mg/l			% COD Removed by Ozone	Ozone Consumption, Lbs/1000 gal.	% of Initial Ozone Feed in Exit Gas
				Raw Effluent	After Filter	Ozone Treated			
Totowa, N.J.	Counter-current column	None	43	82	60	13	78	1.6	21
		None	21-45	112	67	24	64	1.6	21
		Alum	23	89	26	16	38	1.4	38
Berkeley Heights, N.J.	Six-stage cocurrent	Alum +Acid	23	96	41	15	63	0.74	24
		Alum +Acid	11	91	36	17	53	0.53	40

Economic evaluations of ozone treatment of secondary effluents indicate that ozone treatment is competitive with activated carbon systems. Operating costs are highly dependent on plant size and the quality of effluent received. Effluents having high organic content are most economically treated by a combination of chemical clarification and ozonation. Effluents with a low organic content require only ozonation. The need for clarification would roughly double the plant investment and operating costs. Operating costs are 7.7¢/1000 gal. for a 10-million GPD ozone treatment plant without a clarification step, and 15.8¢/1000 gal. if clarification is required. The capital investment is $1,080,000 without clarification, and $2,270,000 with clarification. Activated-carbon treatment cost for a 10-million GPD plant without pretreatment has been estimated at 8.3¢/1000 gal.[1] Capital investment for a plant of that capacity is $1,670,000. Pretreatment requirements for the activated carbon and the ozone treatment plants appear to be similar.

There would be a good potential for cost reduction in the generation of ozone if ozone treatment were to find application on a large scale. A 20% reduction in ozone generation cost would result in a 10% reduction in treatment cost and investment. Since the present efficiency of commercial ozone generators is only 10%, there is considerable potential for such reductions in ozone generation costs.

Because of the promising results in the pre-pilot stage, this development should be continued with a larger-scale pilot plant.

The function of the pilot plant would be to:

1. Establish the effect of scale-up on:

    a) Material transfer;

    b) Ozone-utilization efficiency;

    c) Final TOC, COD, etc., related to initial values[2];

    d) Long-term effects of solid surfaces on ozone decomposition and on operating problems;

    e) Effects of pretreatment on efficiency and on operating problems.

2. Conduct operations over a long enough time to evaluate the effects of hourly, daily, and seasonal changes in the composition of the effluent.

3. Establish the economics of the process more firmly by optimizing the number of stages, residence time, and pretreatment.

4. Obtain data for the design of full-scale plants.

5. Develop specific items of equipment, such as ozone dispersers, etc.

6. Develop methods of control and evaluation.

7. Develop oxygen-recycle systems.

8. Determine the effects of the treated effluent on the streams into which it is emptied.

BLANK PAGE

INTRODUCTION

The accelerated population growth in the United States and the increasing concentration of the population in large urban centers have created a new order of magnitude in the problem of waste-water disposal. Existing methods of waste-water disposal are, in many cases, so inadequate that natural bodies of water into which waste water is discharged are so polluted that they constitute health hazards. For example, many rivers into which wastes are discharged also serve as sources of drinking water for populations downstream from the discharge point. If the assimilative capacity of these rivers is overburdened, conversion of their waters for drinking purposes becomes increasingly difficult.

Conventional, secondary, waste-treatment methods do not remove all of the complex mixture of dissolved and suspended organic matter. Flocculation and filtration of secondary effluents, prior to tertiary treatment, is well advanced and appears capable of giving a product of relatively low solids and colloidal organic content. However, many pathogenic organisms and some organics that cause odor and color will pass through both of these treatments. Present and future quality criteria for water reuse and waste-water discharge will force the adoption of additional or improved treatment methods.

Oxidative purification with ozone, as a tertiary treatment for sewage, has a number of inherent advantages. Ozone's high reactivity permits oxidation, in a continuous process, of many compounds which resist biological oxidation. Ozone removes odor and color. It also destroys pathogenic organisms. After ozonation, chlorine demand is considerably reduced, thus eliminating the tastes and odors produced by chlorination of some residual organics in typical discharged effluents. This is an important consideration in case of water reuse.

The principal disadvantage to the use of ozone for tertiary treatment has been the expense. The high cost of ozone generation requires a high ozone-utilization efficiency if ozone treatment is to be economically competitive. The purpose of this study was to develop experimentally a conceptual design of a process for the treatment of secondary effluents from municipal waste-treatment plants and to evaluate process costs.

The initial development plan included the following aspects:

1. Design, construction and operation of a laboratory-scale (about 10 gal/hr) counter-current column, with auxiliary equipment, for treating secondary effluents with ozone.

2. Monitoring the performance of the ozonation by measuring changes of COD (chemical oxygen demand) and TOC (total organic carbon) of the water, relative to the ozone consumption.

3. Demonstration of the performance of the ozonation process with actual effluents from local sewage-treatment plants.

4. Determination of the efficiency of various tower modifications, packings, and gas-dispersion means.

5. Investigation of the significant parameters of the process, such as gas and liquid velocities, contact time, pressure, pH, ozone concentration, initial organics content of the effluent, and the effect of various clarification pretreatments.

6. Obtaining reaction rate information with respect to changes in impurity level and in ozone consumption, both for use in designing larger-scale plants and for optimization studies.

7. Development of a full-scale process concept, followed by a preliminary evaluation of its cost.

EXPERIMENTAL WORK

The apparatus and tests were chosen to show the effectiveness of ozone treatment in reducing the COD to about 15 mg/l. This is the COD level of a good-quality surface water.

Ozone has been used in the past for drinking-water sterilization. However, Airco had also conducted preliminary tests on ozone treatment of secondary effluent[3]. The various experimental ozone-treatment systems chosen for the present work were designed to extend the available knowledge of existing ozonation processes[4] to eventual large-scale treatment of secondary sewage-plant effluent. By studying chemical reaction rates and the effect of mass transfer of ozone from the gaseous to the aqueous phase, a design concept was obtained for the most economical treatment of secondary effluent with ozone.

Initially, a continuous, countercurrent, reaction system was investigated using an 18-foot glass column, 4 inches in diameter. The effluent, flowing down, was the continuous phase. Bubbles of ozone in oxygen rose from a sparger at the bottom. In order to prevent back mixing, the column was filled with 3/8-inch Raschig rings. The experiments showed that the ozone transfer rate of this type of contacting was not very high.

As a result, we decided to make kinetic studies in a batch reactor. Batch-reaction tests were made by dispersing a stream of ozone into effluent contained in a glass round-bottom flask or in a cylindrical resin flask. The amount of oxidation, characterized by COD and TOC reduction, was measured as a function of time. Important variables were:

1. Type of clarification applied to the effluent prior to ozonation.

2. Type of agitation: High-shear versus low-shear.

3. Ozone concentration in oxygen.

These measurements provided basic reaction-rate data for equipment design. For example, we found that high shear roughly doubles the rates of COD and TOC reduction.

Clarification was included because the effluent contained suspended matter which could easily be removed by coagulation, followed by sand filtration. The clarification facilities enabled us to evaluate the combination of clarification and ozonation, compare the combination with ozonation alone, and explore the effect of various coagulants on ozonation. Ozone consumption was considerably reduced by prior clarification. Clarification removes part of the TOC that is resistant to oxidation by ozone, resulting in a lower final TOC level.

Because the reaction between dissolved ozone and many of the organic compounds to be removed is slow, and because ozone has a limited life in aqueous solution, we concluded that the best treatment of secondary effluent with ozone would be multi-stage, high-shear, gas-liquid contacting.

In each stage, only the amount of ozone that can be expected to react was introduced. Because the half-life of ozone in water is about 20 minutes, we chose a residence time of 10 minutes per stage. About one hour was needed for a COD reduction from about 35 or 40 mg/l to 15 mg/l. Therefore, a six-stage system was selected for the concept.

The six-stage system was simulated by recycling effluent through the 18-foot column. Ozone in oxygen, and effluent, were mixed in an injector which provides a low-cost form of high-shear contacting. From the injector, the mixture descended a 20-foot dissolving tube, entered the bottom of the column, and then rose through the packing. The liquid overflowed at the top of the column and was pumped back to the injector. Ten minutes were required for passage of the liquid around the circuit. Thus, ten minutes of operation represented the performance of one stage. In one hour, a six-stage system was simulated.

The rate curves obtained from experiments with the batch reactor, equipped with the high-shear turbine agitator, could be used as a design basis for the 6-stage continuous system. From the experimental curves of COD and TOC reduction versus time, the amount of ozone to be directed to each stage could be estimated. In this way, an overall ozone efficiency as high as 90% was obtained.

The experiments outlined above are described in detail in the sections that follow.

Analytical Procedures

The methods used for sample preparation were adopted from "Standard Methods for the Examination of Water and Wastewater"[5]. Samples of 200 ml were taken for TOC, COD, and ammonia-nitrogen

analyses. The sample bottles either had glass stoppers or screw caps with inert plastic liners. Each sample was acidified with 5 ml of 10% sulfuric acid to stop biological action; this gave the sample a pH of about 2.

COD Determination[6] was made using the dichromate method.

TOC Determination was made with Beckman Carbonaceous Analyzer, Model 137879 U. The methods given in the instruction manual for this instrument were followed. Potassium biphthalate, instead of acetic acid, was used for preparing solutions to standardize the instrument.

Turbidity was measured with a Hach "DR" colorimeter-turbidimeter. The scale was calibrated in Jackson Turbidity Units (J.T.U.). Standards were made up by mixing equal volumes of a solution consisting of 1 g of hydrazine sulfate in 100 ml of water and a solution consisting of 10 g of hexamethylene tetramine in 100 ml of water. The mixture was allowed to stand overnight. Dilution of 1 volume of that mixture with 99 volumes of water gave a turbidity of 40 J.T.U. Further dilution of the 40 J.T.U. standard with an equal volume of water gave a 20 J.T.U. standard, etc. No correction was needed for the scale readings of the Hach instrument. The standards and the Hach turbidimeter readings were compared with a Brice-Phoenix, Universal, Light Scattering Colorimeter. The readings from the Hach instrument were more consistent than those from the Brice-Phoenix Colorimeter because the light scattering from both the standards and effluents varied with the light angle. This asymmetric behavior caused relatively large errors in the light scattering measurements.

Ammonia-nitrogen was determined by direct Nesslerization[7].

Ozone was determined in effluents and gases by the iodometric method, as follows:

Gas streams were passed through a fritted-glass sparger in a gas absorber containing 300 ml of water and 100 ml of 10% KI solution. One-half cubic foot of gas was measured through the absorber by a wet test meter connected downstream. A 25-ml sample was pipetted from the 400 ml of solution; 25 ml of 10% sulfuric acid and 50 ml of distilled water were added, and the iodine was titrated with standard 0.1N thiosulfate solution.

Ozone in liquids was determined by adding 400 ml of sample to a mixture of 20 ml of 10% KI solution, 20 ml of 10% sulfuric acid, and 60 ml of water (all) in a 500-ml glass-stoppered graduate. The entire 500 ml was titrated with standard 0.1N thiosulfate solution.

Gaseous impurities in exit gas and oxygen samples were analyzed with a gas chromatograph after removal of ozone and water vapor.

Secondary Effluent Composition

Effluents from the final clarifier of a secondary waste-treatment plant had the following characteristics:

Color		Pale Straw
Odor		Variable
Chemical Oxygen Demand	(mg/l)	70-150
Total Organic Carbon	(mg/l)	20-50
Ammonia Nitrogen	(mg/l)	5-30
Turbidity (Jackson Turbidity Units)		30-60

Normally, the effluent contains enough residual detergent to foam easily.

Initially, we thought that ammonia would react with ozone. Therefore, a special low-ammonia effluent was obtained from the waste-treatment plant of the Totowa, New Jersey, Training School. Later we switched to effluent from the municipal waste-treatment plant of Berkeley Heights, New Jersey.

Ozonizer

Ozone was generated in a stream of pure (>99.5 wt%) oxygen with a Welsbach, "T-23", laboratory, ozone generator. This unit can produce 5 grams of ozone per hour from pure oxygen. It will give a concentration of about 3.6% ozone, by weight, in an oxygen flow of about 100 liters per hour. Lower concentrations are obtained by increasing the oxygen flow or reducing the voltage.

Solubility and Decomposition of Ozone in Water

Ozone is about 13 times more soluble in water than oxygen. The solubility of pure ozone is reported to be between 0.57 and 0.8 g/l at 20°C. At saturation, an aqueous solution in contact with oxygen containing 2 wt. % ozone will contain about 11 mg O_3/l and 40 mg O_2/l. The instability of ozone makes measurements of its solubility and decomposition rate difficult. The information given in the literature varies considerably[8,9,10,11].

The solubility and decay rate of ozone in water were checked by sparging ozone into water for different periods of time. The solution was sampled and analyzed for ozone by the

iodometric method at different times after ozone introduction had been stopped. The results of these tests gave an ozone solubility, at equilibrium with 4 wt.% ozone in oxygen, of 10 mg/l at 25°C starting with distilled water. Decay rates were 25% in 30 minutes, and 60% in 60 minutes. In tap water, under similar conditions, the solubility was 6 mg/l. Decay rates in tap water were 75% in 30 minutes, and 87% in 60 minutes.

In a later stage of this project, solubility of ozone in clarified secondary effluent was determined by sparging 1.56 wt.% ozone in oxygen into secondary effluent in a cylindrical resin kettle using a high-shear turbine stirrer. Samples of the effluent were withdrawn into KI solution after 10 minutes of ozone treatment, and again after 60 minutes; and each sample was titrated. The 10-minute sample contained 7.2 mg O_3/l, and the 60-minute sample 8.4 mg/l. Adjusted to 4 wt.% ozone in oxygen according to Henry's law, this would be equivalent to 21.6 mg/l of ozone - a much higher value than the 10 mg/l determined earlier. The higher value also approaches the solubility of ozone given by Yost and Russell[11]. Better agitation was probably responsible for the higher dissolved-ozone values obtained in the later work. Ozone dissolved more rapidly, and thus more was in solution to react with KI before the ozone could decompose. Tap water also may contain substances which decompose ozone.

Clarification of Secondary Effluents

A secondary effluent normally contains suspended organic matter, part of which can be removed by sand filtration. Additional colloidal matter can be removed by chemical clarification (i.e., coagulation and settling, followed by filtration). Coagulation and filtration are generally less costly than ozone treatment on a COD removal basis. Therefore, the burden on the ozone treatment can be profitably decreased by a clarification pre-treatment. A schematic flow diagram of the clarification equipment is shown in Figure 1.

All secondary effluents used in this investigation were filtered through a sand bed, 9 inches deep, laid on a 6-inch layer of graded stone in a 20-gallon stainless steel tank. The filter was fed by gravity at a uniform rate from a 20-gallon open feed tank equipped with a variable-speed paddle mixer. The effluent was spread over the surface of the sand by a perforated distributor ring. An outlet in the side of the filter tank, and located a few inches above the sand surface, served as an overflow for the backwash. The sand was backwashed with a large volume of tap water; and its surface was cleaned by scraping, if necessary, at the end of each day's runs.

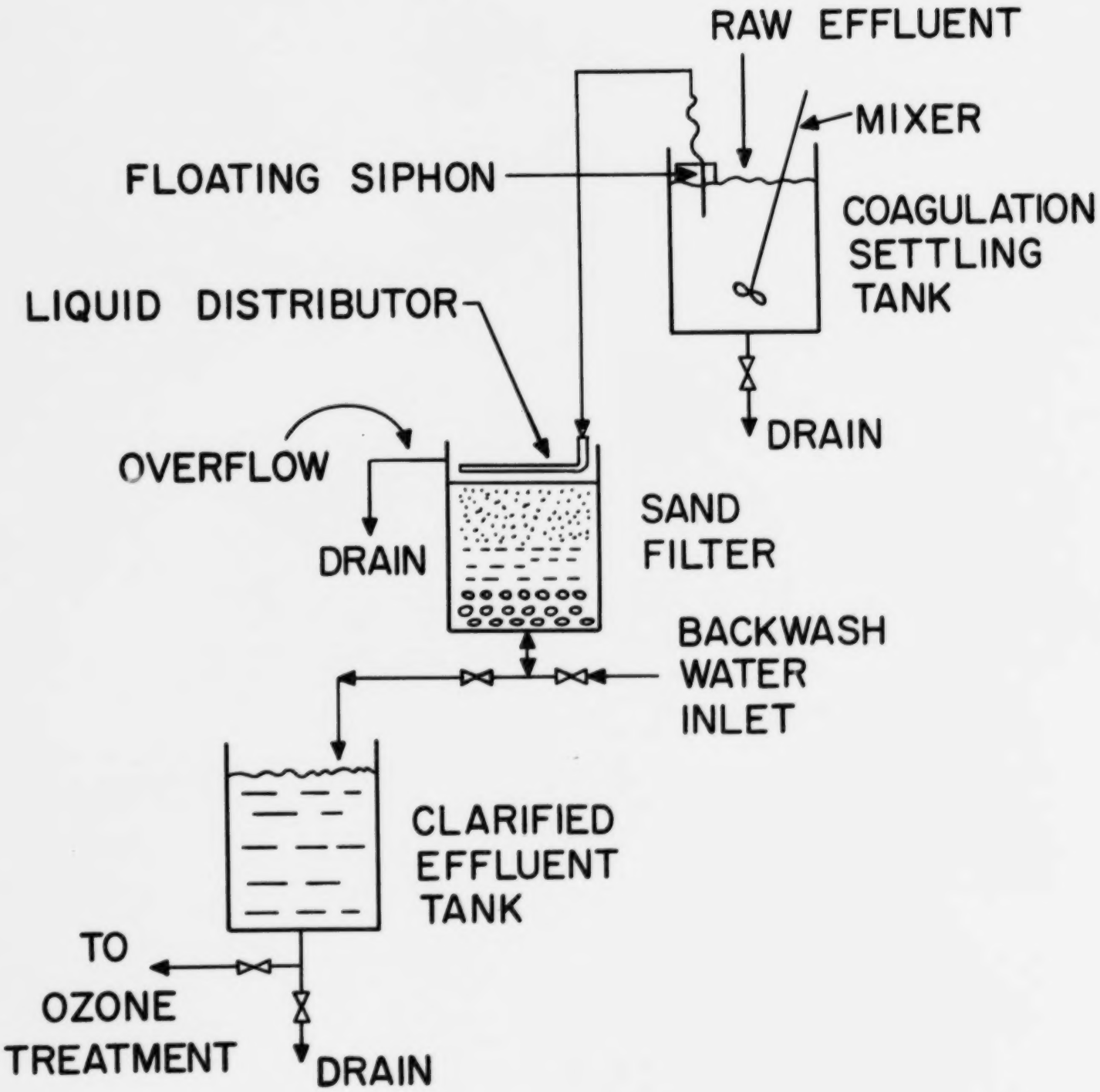

Figure 1. Schematic flow diagram of the coagulation - filtration equipment.

The selected dosage of each coagulant was within the range normally used for water treatment. The action of the alum, which was the first one tested, was initially observed on a one-gallon sample of effluent in a glass jar equipped with a low-speed laboratory stirrer. The 132-mg/l dosage seemed to produce a satisfactory floc and did not increase the dissolved solids content of the filtered effluent excessively. This dosage was then tried in the 20-gallon apparatus (see Figure 1) with good results. Lime was compared with alum as a coagulant. We estimated that a lime dosage of 396 mg/l would give results equivalent to 132 mg/l of alum. However, this was enough lime to produce a high pH which might increase spontaneous decomposition of the ozone. Consequently, a lime dosage of 132 mg/l was also tried. In addition, alum-lime and alum-sulfuric acid combinations were tested to provide a full range of pH levels (see Table II).

Alum was added as a 2.5% solution, and lime as a powdered hydrate. In both instances, the effluent in the tank was stirred vigorously. After 5 minutes, the stirring was slowed down, and very gentle agitation was continued for 30 minutes. The stirring was stopped, and the floc was allowed to settle for 30 minutes. The effluent was then drawn out from one inch below the liquid surface with a floating siphon and was put through the sand filter.

In earlier runs, the coagulation period was longer, and the settling was omitted. Settling reduced the possibility of breaking the floc on the filter and improved TOC and COD removals slightly.

Differences among the various coagulants were usually not significant with respect to TOC and COD removals (see Table III). Most of the coagulant treatments removed about 60% of the COD from the raw effluent, with the exception of some of the lower lime dosages which removed only about 40%. The greatest difference was in the pH of the treated effluents. The high lime dosage gave a high pH, and the alum-acid coagulants gave the lowest pH.

Another way of characterizing coagulation is by measuring turbidity change. Table III also shows how turbidity changed with coagulation. Turbidities were measured with a Hach "DR" Turbidimeter and were expressed in Jackson Turbidity Units.

TABLE II

EFFECT OF COAGULANT ON pH OF CLARIFIED EFFLUENT AND OF OZONE-TREATED PRODUCT

Coagulant	Dosage, mg/l	Average pH		
		Raw Effluent	After Clarification	After Ozone Treatment
$Ca(OH)_2$	396	7.2	10.9	9.6
$Ca(OH)_2$	132	7.3	8.7	8.0
$Ca(OH)_2$ +$Al_2(SO_4)_3$	132 66	7.5	8.8	7.4
$Al_2(SO_4)_3$	132	7.5	6.8	7.8
$Al_2(SO_4)_3$ +H_2SO_4	110 63-92	7.4	5.8	6.6

TABLE III

REDUCTIONS OF COD AND TOC BY CLARIFICATION OF BERKELEY HEIGHTS EFFLUENTS

Coagulant Dosage, mg/l	Coagulated and Filtered						Coagulated, Settled, and Filtered							
	TOC, mg/l			COD, mg/l			TOC, mg/l			COD, mg/l			Turbidity, J.T.U.	
	Raw Effluent	After Filter	Percent Removed	Raw Effluent	After Filter	Percent Removed	Raw Effluent	After Filter	Percent Removed	Raw Effluent	After Filter	Percent Removed	Raw Effluent	After Filter
$Ca(OH)_2$ - 396	20	10	50	75	32	57	30	11	63	87	30	66	60	8
$Ca(OH)_2$ - 132	25	11	56	85	36	58	26	16	39	73	40	45	39	8
$Ca(OH)_2$ - 132 $+Al_2(SO_4)_3$ - 66	22	9	59	81	34	58								
$Al_2(SO_4)_3$ - 132	23	14	39	117	47	60	30	11	63	90	33	63	46	6
$Al_2(SO_4)_3$ - 110 $+H_2SO_4$ - 63	21	12	43	85	39	54	29	11	62	91	36	60	49	9
None	29	22	24	111	68	39							40	21

OZONATION IN A CONTINUOUS COUNTERCURRENT COLUMN

The most obvious means of ozone transfer from oxygen to effluent is countercurrent contacting. The experiments discussed below were designed to evaluate the efficiency of this process.

Equipment and Procedures

A flow diagram of this system is shown in Figure 2. Oxygen, containing 1.6 to 3.6 wt.% ozone, was fed continuously through a stainless steel sparger into the bottom of an 18-foot glass column, 4 inches in diameter. Effluent was pumped continuously from the filtrate receiving tank through a flow meter into the top of the column. It flowed down the column countercurrently to the rising gas bubbles. Treated effluent flowed up the outflow leg to an overflow tee located at the same level as the liquid surface in the column. Thus, the effluent was the continuous phase in the column.

In the first tests, the column was not packed. Agitation by the gas bubbles produced so much turbulence that a high percentage of the effluent by-passed to the bottom. As a result, part of the effluent escaped full treatment; and behavior of the system was erratic. The column was then filled with 3/8-inch porcelain Raschig rings to prevent back-mixing. The packed column was used for all of the runs reported herein.

The duration of most of the tests was about 6 hours. Samples of liquid were taken from the bottom of the column at 30-minute intervals for TOC, COD, ammonia-nitrogen, and dissolved-ozone analyses. The gas leaving the top of tower was analyzed for ozone by passing it through an absorber containing KI solution and then through a wet-gas meter. A complete analysis of the gas leaving the top of the tower was carried out during run 85. A sample of the oxygen, fed to the ozone generator, was analyzed at the same time. The results are given in Table IV. The carbon dioxide content corresponds to about one atom of oxygen per ozone molecule reacting to carbon dioxide for 75% of the entering ozone. About one-third of the nitrogen content in the exit gas might have been stripped from the water as dissolved nitrogen. The balance of the nitrogen was probably due to air leakage and some other forms of nitrogen in the effluent.

In most of the early tests (56-76), an effluent from the sewage-disposal plant of the Totowa, New Jersey, Training School was used. The ammonia-nitrogen content of this effluent was low, about 5-10 ppm. Originally, low-ammonia effluent was chosen in the belief that ammonia would consume ozone and confuse the test results. However, the ammonia level decreased very little during ozone treatment. After independently verifying this with ozone treatment of an ammonium sulfate solution, permission was obtained to use Berkeley Heights, New Jersey, effluent which contained 10-30 ppm of ammonia-nitrogen.

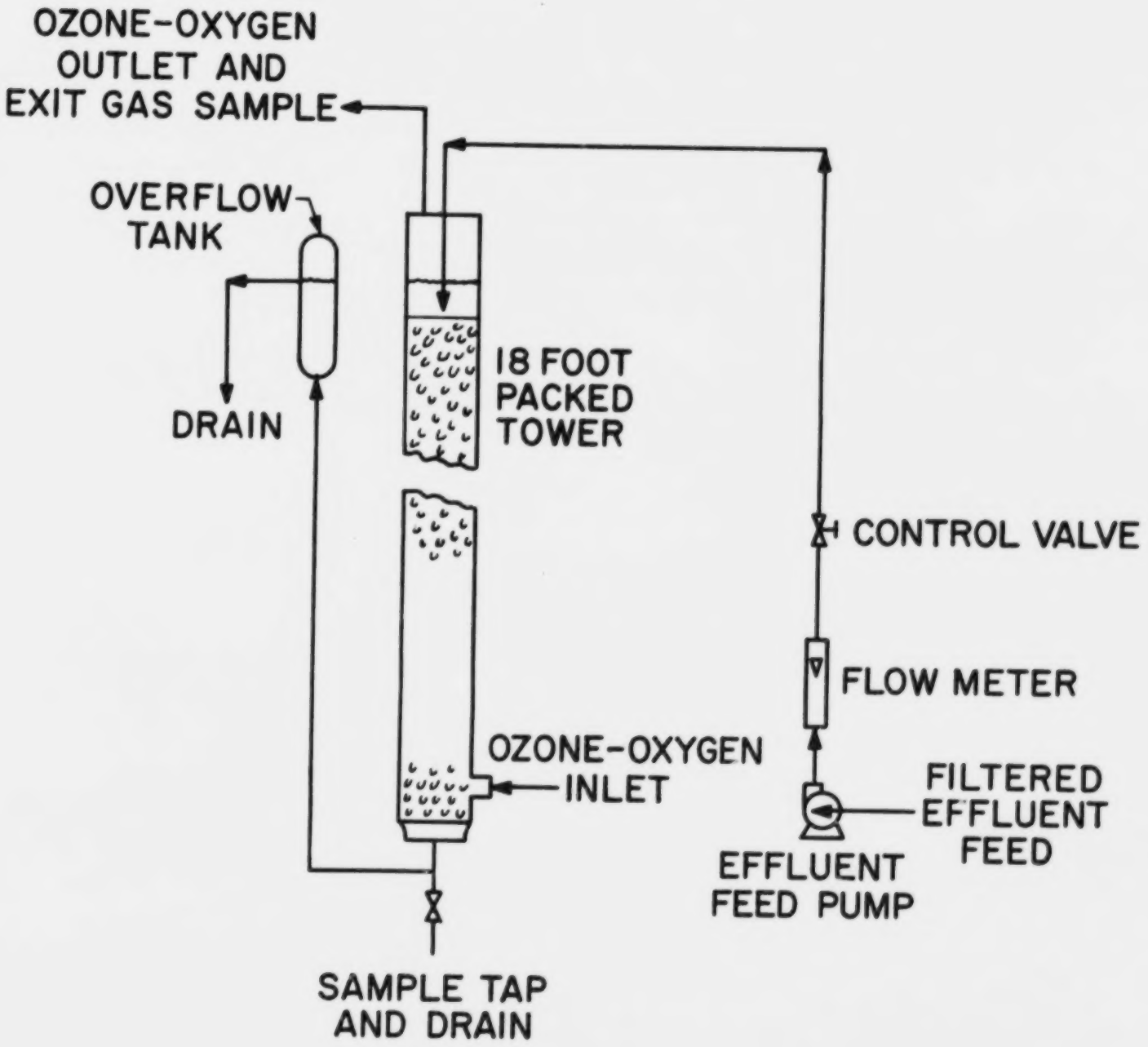

Figure 2. Schematic flow diagram of continuous countercurrent ozonation.

TABLE IV

CONTINUOUS COUNTERCURRENT OZONATION:
COMPLETE ANALYSIS OF THE EXIT GAS FROM THE COLUMN IN RUN 85, AND OF THE OXYGEN USED IN THAT RUN

	Oxygen, ppm (V/V)	Exit Gas*, ppm (V/V)
Carbon Dioxide	<1	9450
Nitrogen	5	9300
Methane	10.3	<8.0
Acetylene	0.07	<0.01
Propylene	0.02	<0.01
n-Butane	0.04	<0.01
Isobutane	0.02	<0.01
Nitrous Oxide	1.1	1.5
Xenon	0.45	0.36
Krypton	7.2	5.0

* Moisture and ozone removed before analysis.

The effect of pH was tested by adding sulfuric acid or sodium hydroxide to the filtered feed in runs 70 and 76, respectively.

At the end of run 76, a sample of the ozone-treated effluent was drawn from the outlet of the column into a sterile container. This sample was sent to a local water-testing laboratory for chemical and bacteriological examination. The results are given in Table V. The sample meets the PHS standards for potable water. Actually, run 76 was not one of the best runs. Even better results can be expected with ozone-treated water of later runs.

Results and Discussion

In the early work with the Totowa effluent, different liquid flow rates, initial COD levels, and pH levels were tested. Table VI gives a summary of these results.

The COD and TOC efficiency indices given in this and the following tables are expressed as the ratios of COD (or TOC) removed to the molecular equivalents of ozone fed into the process. It is assumed that one atom of oxygen in each ozone molecule is used in oxidation of organics, while the other two are lost as molecular oxygen. Thus, the definitions are:

COD/ozone efficiency index =

$$\frac{\text{COD removed (mg/l)}}{\text{1/3 of ozone supplied (mg/l effluent)}} \times 100\%$$

TOC/ozone efficiency index =

$$\frac{\text{TOC removed (mg/l)}}{\text{1/8 of ozone supplied (mg/l effluent)}} \times 100\%$$

If more than one atom of oxygen per ozone molecule reacts, or if some of the oxygen carrier gas takes part in the oxidation, the efficiency indices can be over 100%.

In runs 58 and 60, where the COD was reduced to 5 mg/l, the residence time was 1.8 hours which was considered excessive. The gas leaving the tower contained 34% of the ozone fed, making the COD efficiency index low. In runs 66 and 68, a large excess of COD was fed, resulting in high COD/ozone efficiency indices and lower ozone contents in the exit gas. However, the treated effluent had a high COD. In runs 70-76, a flow rate was used which gave a 0.9-hour effluent residence time. Approximately 30-35% excess ozone was fed. The results at pH = 7 seemed to be slightly better than those at higher and lower pH levels. Under these

TABLE V **WATER ANALYSIS**

WATER FROM Experimental Work DATE COLLECTED February 5 19 68

Sample No. 1 Source — Lab. No.
Sample No. 2 Source
Sample No. 3 Source Tertiary Sewage treated with Ozone Run 76
Sample No. 4 Source
Sample No. 5 Source
Sample No. 6 Source
Sample No. 7 Source
Sample No. 8 Source

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
PHYSICAL ANALYSIS - P.P.M.								
Color			2					
Turbidity			.15					
Odor {Hot			Trace	Sep.				
Odor {Cold			0					
Taste			---					
CHEMICAL ANALYSIS - P.P.M.								
Alkalinity to Phenolphthalein								
Alkalinity - Total			128					
Hardness - Total ($CaCO_3$)			122					
Free CO_2			---					
Total Solids			208					
Manganese (Mn)			0					
Iron (Fe)			Trace					
Iron & Aluminum Oxides (R_2O_3)			---					
Calcium (Ca)			---					
Magnesium (Mg)			---					
Chloride (Cl)			---					
Fluoride (F)			---					
Sulfates (SO_4)			---					
pH			7.9					

BACTERIOLOGICAL ANALYSIS	Quantity of Water Tested - ml.																							
	0.1	1	10	0.1	1	10	0.1	1	10	0.1	1	10	0.1	1	10	0.1	1	10	0.1	1	10	0.1	1	10
Gas in Lactose Broth									0/5															
Gas in Brilliant Green Bile									0/5															
Coliforms Present								None																
Bacteria per ml.(37°C)								0																
Millipore Count/ 100 ml								0																

REMARKS: Bacteriological Examination indicates water to be free of Coliform Bacteria and to meet PHS standards for potable water. Physical Examination Color is minimal, clarity good, odors meet acceptable standards. Chemical tests using very small aliquots(giving too great a margin for error) show sample as meeting acceptable quality standards.

Examined at 259 Woodland Ave, Summit, N.J. D. J. MacGowan
Analyst

Date February 12, 1968

Form W-132

TABLE VI

CONTINUOUS COUNTERCURRENT OZONATION OF TOTOWA EFFLUENTS

Run No.	Effluent Flow, l/hr.	pH after filter	Ozone in Gas feed, mg/l*	O_3 Balance, %			TOC, mg/l			COD, mg/l			Efficiency Indices, %		Ammonia - N, mg/l		
				Used & Decomposition In Tower	In Effluent Leaving Tower	In Exit Gas	Raw Effluent	After Filter	Ozone Treated	Raw Effluent	After Filter	Ozone Treated	TOC/ozone	COD/ozone	Raw Effluent	After Filter	Ozone Treated
56	22.7	7	43	67	6	27	29	26	6	105	73	16	84	90	3	3	5
58	11.4	7	45	62	4	34	38	30	4	115	85	5	52	60	8	6	7
60	11.4	7	45	64	3	33	30	25	4	112	84	5	42	59	9	6	5
62	34.2	7	43	73	5	22	45	29	22	158	101	57	44	128	-	-	-
64	34.2	7	47	70	6	24	40	28	20	154	101	41	46	130	7	5	4
66	11.4	7	47	88	1	11	91	59	26	359	267	64	63	146	-	-	28
68	11.4	7	47	84	2	14	85	45	28	340	179	64	33	83	-	-	-
70	22.7	5	45	69	5	26	25	15	8	90	60	13	28	70	9	10	8
72	22.7	7	43	72	7	21	23	15	6	82	60	13	38	74	12	6	7
74	22.7	7	49	80	4	16	44	26	14	157	72	19	44	73	-	-	-
76	22.7	9.5	45	75	6	19	24	14	8	102	65	23	23	62	18	11	11

*Gas Flow: 102 liters/hr at 22°C, 760 mm of Hg, in all runs.

conditions, the exit gas contained about 20% of the ozone fed, the COD/ozone efficiency index was about 70%, and the treated effluent had satisfactory TOC and COD levels.

The ammonia-nitrogen content of the effluent was not affected by ozonation in any of these tests. To investigate this further, a solution of ammonium sulfate equivalent to a nitrogen content of 28 mg/l was treated with ozone in the tower under the same conditions as had been used in run 76. Two 6-hour tests were run, and the ammonia-nitrogen content of the treated samples varied between 24 and 29 mg/l, indicating that ozone did not react appreciably with the ammonia.

Berkeley Heights effluent was used for the next group of tests which were intended to test the effect of clarification pretreatments on ozonation. The results are given in Table VII, together with the results of runs without clarification pretreatment.

Both the Totowa and the Berkeley Heights waste-treatment plants used a trickling filter for secondary treatment. The throughput in the Totowa trickling filter, expressed as a percentage of rated capacity, was lower which may be the reason why the Totowa effluent is somewhat more amenable to ozone treatment. Some substantiation for this may be the lower TOC and COD levels that were obtained with Totowa effluent after ozonation. With Berkeley Heights effluent, no satisfactory COD levels were reached without a clarification pre-treatment. We also noticed that, with the approach of spring, the COD levels in the Berkeley Heights secondary effluent decreased from about 115 to 85 mg/l. Warmer weather increased the efficiency of the secondary treatment.

The ozone efficiency indices decrease with decreasing TOC and COD levels of the secondary effluent, indicating that the most-readily bio-oxidizable organic compounds in the effluent also consume ozone most efficiently. It is much more difficult, for example, to reduce the COD from 25 to 15 mg/l than from 65 to 55 mg/l. Figure 3 shows a correlation between the COD/ozone efficiency index and the COD of the column feed. It appears relatively independent of the type of coagulant used. The correlation is affected, however, by the liquid residence time in the column.

A high dosage of lime coagulant (runs 94 and 95) raised the pH in the column to 10.6. During ozonation, a gradual decline in the ozone level in the tower was noticed. After 3 hours, no ozone could be found in the effluent from the bottom of the tower and very little in the exit gas. This was possibly caused by the gradual build-up of an alkaline deposit that actively decomposes ozone. The lower dosage of lime (runs 96 and 97) showed signs of decomposition catalysis, but operation was much better. Another effect of the high pH (runs 94 and 95) was a drastic reduction of the ammonia-nitrogen content which may have caused part of the loss of ozone.

TABLE VII

CONTINUOUS COUNTERCURRENT OZONATION OF BERKELEY HEIGHTS EFFLUENTS

Run No.	Day*** of the Week	Ozone in Gas Feed, mg/l	Coagulant, mg/l	Average pH in the Column	TOC, mg/l			COD, mg/l			O_3 Balance, %			Efficiency Indices, %		Ammonia-N, mg/l		
					Raw Effluent	After Filter	Ozone Treated	Raw Effluent	After Filter	Ozone Treated	Used + Decomp. in Tower	In Effluent Leaving Tower	In Exit Gas	TOC / Ozone	COD / Ozone	Raw Effluent	After Filter	Ozone Treated
77*	3	45	None	7.4	28	28	11	110	-	20	70	6	24	70	-	21	15	14
78*	5	47		7.4	32	26	11	156	-	21	74	6	19	57	-	26	21	20
79*	4	44		7.4	27	13	10	94	-	26	73	6	22	15	-	28	23	20
85*	3	44		7.4	22	20	14	120	90	34	86	4	10	22	86	31	25	26
86*	4	44		7.4	20	20	8	118	88	-	82	5	14	44	-	28	24	23
87*	1	40	Alum-132	6.9	35	16	12	118	49	23	81	6	14	17	43	30	23	24
88*	3	44		7.0	17	15	4	119	46	19	71	6	23	41	42	31	19	20
89*	5	44		7.0	18	11	6	114	46	13	70	6	24	19	51	26	20	21
90**	2	22	None	7.4	35	21	11	105	59	29	77	4	19	45	54	29	16	23
91**	3	22		7.4	18	11	7	75	36	17	56	5	39	20	36	10	5	6
92**	4	23	Alum-132	7.0	25	12	7	88	24	17	54	5	41	26	14	14	13	14
93**	5	23		7.0	25	11	5	91	28	15	60	5	35	27	22	19	18	19
94*	1	48	Lime-396	10.6	18	10	6	70	29	15	86	4	10	14	19	11	8	4
95*	2	47		10.6	21	11	6	80	36	10	95	2	3	18	36	11	12	2
96*	3	48	Lime-132	8.4	25	12	5	90	38	13	80	7	13	26	38	17	14	12
97*	4	49		8.3	25	11	5	81	35	11	72	8	20	22	32	18	15	11
98*	5	48	Lime-132	8.2	22	10	3	68	35	16	60	8	32	23	27	20	13	10
99*	1	47	+Alum-66	7.9	22	8	5	95	33	16	54	9	37	15	24	19	12	10
100*	2	48	Alum-110 +H_2SO_4-65	6.6	21	12	6	85	39	13	51	8	41	21	32	19	15	12
101*	3	47	Alum-110 +H_2SO_4-92	6.1	25	10	4	89	28	17	29	10	61	20	13	-	-	-
Overall Averages:																		
Without coagulation-				7.4	26	19	10	112	67	24	74	5	21	39	58	25	19	19
With coagulation-				7.8	23	11	6	91	35	15	66	7	27	24	30	19	15	13
Averages for 22-23 mg/l of O_3																		
Without coagulation-				7.4	26	16	9	90	48	23	67	5	29	32	45	20	10	15
With coagulation-				7.0	25	11	6	89	26	16	57	8	35	26	18	16	15	16

*Effluent Flow - 22.7 l/hr.
Gas Flow - 102 l/hr. (22°C, 760 mm Hg)

**Effluent Flow - 22.7 l/hr.
Gas Flow - 170 l/hr. (22°C, 760 mm Hg)

***Day of the week 1 = Monday to 5 = Friday

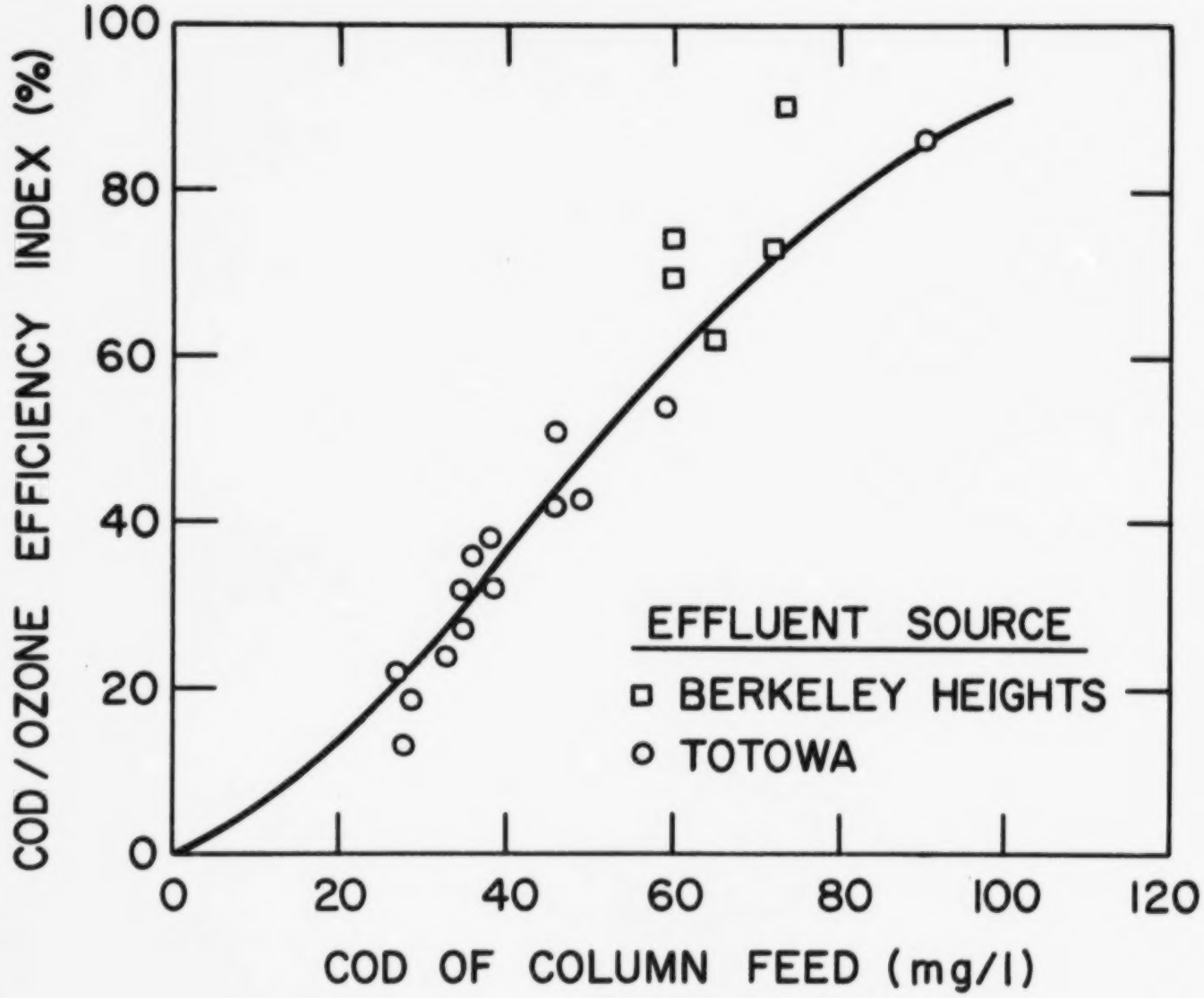

Figure 3. Continuous countercurrent ozonation: COD/ozone efficiency index as a function of COD of the column feed.

The alum-sulfuric acid combination (run 100), which lowered the pH to 6.6, gave excellent TOC and COD removals and a relatively good COD/ozone efficiency considering the high concentration of ozone in the exit gas. Lowering the pH to 6.1 (run 101) increased the ozone concentration in the exit gas still further, but seemed to retard COD removal to some extent.

At the lower ozone concentrations, more gas was supplied, and a higher fraction of the ozone fed left the column in the exit gas. This decreased ozone-absorption efficiency was anticipated.

Summarizing the results of the continuous countercurrent ozonation, we found:

1. Ozonation efficiency of a secondary effluent was high when its COD and TOC were high. However, such an ozonated effluent had an unacceptably high COD and TOC.

2. Berkeley Heights effluent was more difficult to oxidize to a low COD level than was Totowa effluent. However, pre-clarification enabled us to bring the COD of Berkeley Heights effluent from 35 to 15 mg/l after 0.9 hours of treatment with ozone.

3. The pH range from 6.6 to 8.3 seemed to be optimum.

BATCH REACTOR TESTS

Ozonation in the continuous countercurrent column is a combination of mass transfer and chemical reaction. Since we knew neither the relative importance of each of these two steps nor the effectiveness of the column packing for this particular mode of operation, scale-up predictions were difficult to make. Therefore, we decided to make the next fundamental ozonation studies in a batch reactor. The main variables to be investigated were:

1. Agitation rate.
2. Clarification with different coagulants.
3. Ozone concentration in the gas.

Equipment and Procedures

Batch ozonation tests were conducted with both low-shear and high-shear agitation. The low-shear apparatus consisted of a 250-ml, three-necked, roundbottom flask fitted with a porous-glass dispenser for gas introduction and with a low-speed paddle agitator. The high-shear apparatus, shown in Figure 4, consisted of a 2000-ml resin flask fitted with a flat-blade turbine agitator driven at 1200 rpm by an electric motor. Gas, introduced through a 1/4-inch O.D. aluminum tube, was directed to the bottom of the agitator. Liquid samples were withdrawn through 1/4-inch O.D. aluminum tubing. A baffle system was suspended above the agitator to effect proper mixing.

The operating procedures were different for the two types of batch reactors. For the low-shear reactor, batches of fresh effluent were treated with excess ozone for various periods of time, at the end of which the total batch was prepared for TOC and COD determinations by stabilization with a nitrogen purge and addition of acid.

For the high-shear reactor, 2000 ml of fresh effluent (clarified, if desired) were placed in the reactor and treated with excess ozone. Liquid samples were periodically withdrawn and prepared for TOC and COD determination by stabilization with a nitrogen purge and the addition of acid.

Significant differences were noted in the quality of the secondary effluent each day. Varying levels of TOC and COD of the effluent as received, foaming tendencies during testing, and color of the effluent after filtration were indications of these changes. In order to minimize the effects that effluent variability would have on our study of process variables, a series of tests was conducted for each variable, and the arithmetic mean of the results was used.

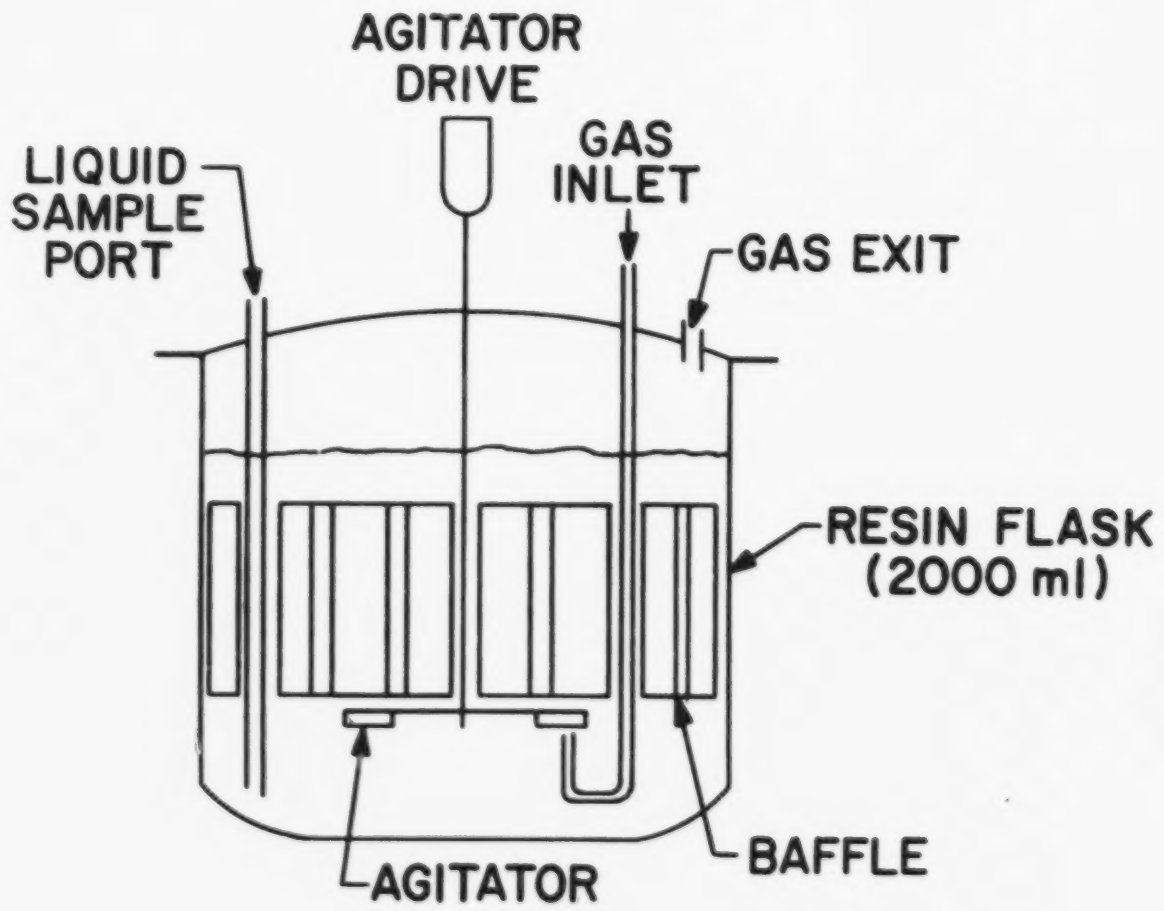

Figure 4. High-shear batch reactor.

Results and Discussion

The overall reaction rate of ozone with organic contaminants in waste water is a combination of the transfer rate of ozone from the gaseous phase to the liquid phase (mass transfer), and the reaction rate of the transferred ozone with the organics. Gas-liquid mass transfer is characterized by the mass transfer coefficient which is unit mass transferred per unit time, unit cross-sectional area and unit driving force. This mass transfer coefficient is described as either gas-film, liquid-film, or combination-film controlled. In mass transfer of relatively insoluble gases such as oxygen or ozone, liquid-film transfer controls. This means that the major resistance to mass transfer is imposed by the presence of a stagnant liquid film, or layer, through which mass transfer must occur[12]. Thus, by increasing the interfacial area between phases and increasing the agitation of the liquid phase so as continually to renew the contact surface exposed to the gas phase, resistance to mass transfer would be reduced. High agitation, coupled with high shearing action, would achieve these requirements.

A comparison of the overall rates of ozonation in the low and high-shear batch reactors is shown in Figure 5 as a plot of TOC versus time. The asymptotic approach of the curve for the high-shear case indicates that part of the TOC is refractory to ozone treatment. Thus, the total TOC content can be thought of as consisting of two general classes of materials: one which is relatively refractory to ozonation, and one which is readily destroyed by ozone. A second set of plots in Figure 5 is shown in which an arbitrarily selected, "refractory fraction" of 30% of the inlet TOC content was subtracted from the total TOC values. The resultant plots are straight lines indicating that the reaction is first-order for the non-refractory part of the TOC. The slopes of the non-refractory TOC levels are 0.027 min^{-1} for the high-shear case and 0.014 min^{-1} for the low-shear. This significant increase in reaction rate realized with increased agitation shows that, for effective ozonation of sewage effluent, good agitation must be considered the prime objective in contactor designs. All subsequent batch-reactor tests were conducted in the high-shear batch reactor.

Dissolved ozone levels were determined for the high-shear batch reactor. The results in Table VIII indicate that the gas-to-liquid transfer rates were greater than the reaction rates.

The value selected for the refractory TOC in the agitation studies was based on the asymptotic approach value of the high-shear runs and was assumed to be equal to 90% of the TOC content remaining after 120 minutes of ozonation. Similar data handling

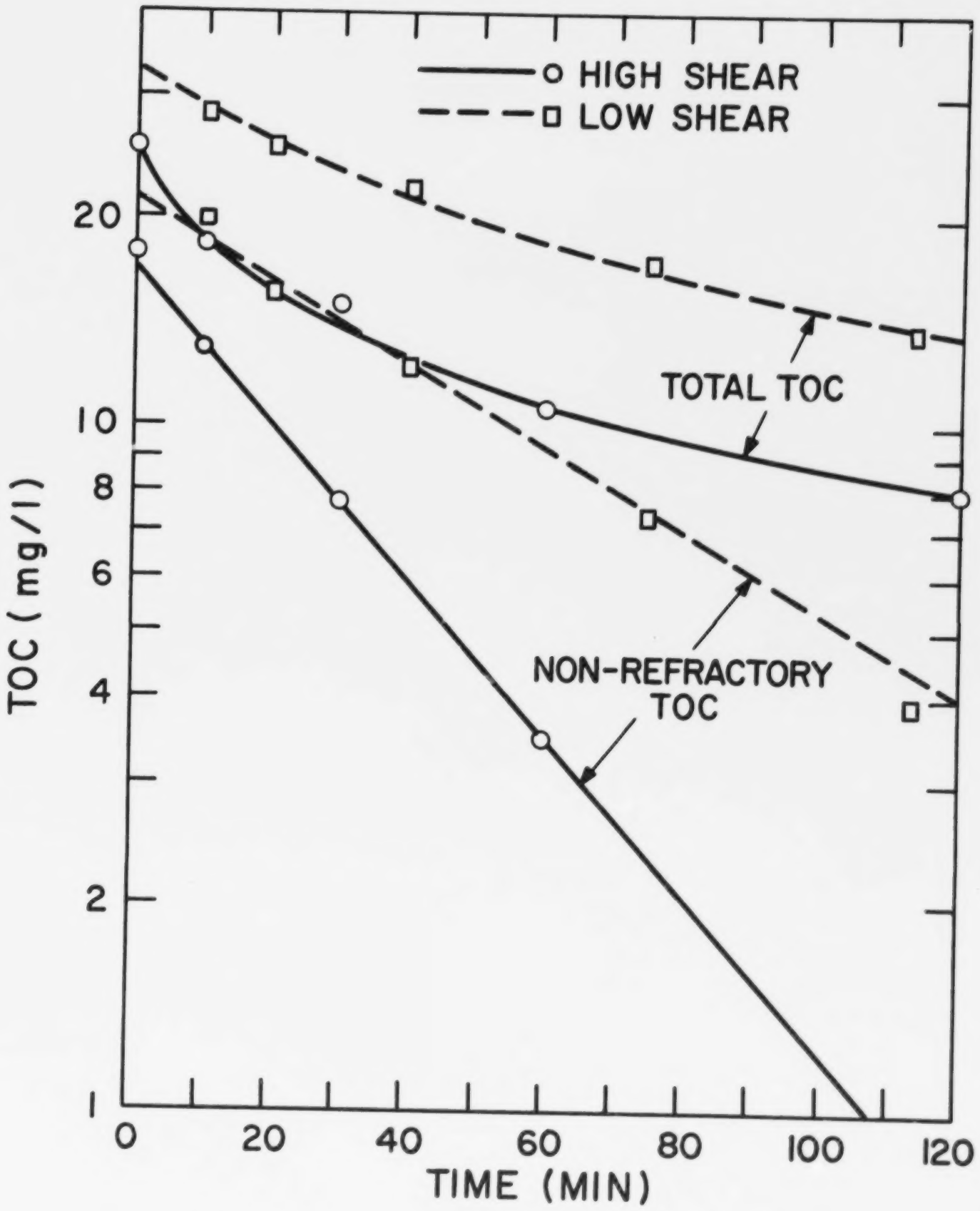

Figure 5. Ozonation in batch reactors: effect of agitation on TOC removal with excess ozone.

TABLE VIII

DISSOLVED OZONE LEVELS FOR HIGH-SHEAR BATCH REACTOR

Time, Min.	Ozone In Gas Feed, mg/l	TOC, mg/l	COD, mg/l	Dissolved Ozone	
				mg/l	% of Saturation
0	22.6	15	28	0.0	0
10	22.6	-	-	7.2	72
60	22.6	7	10	8.4	84

methods for all batch tests resulted in essentially similar results; i.e., plots of the logarithm of non-refractory TOC versus time gave straight lines. In reality, the organic content of most effluents is expected to be composed of compounds encompassing the full range from totally refractory compounds to compounds readily destroyed by ozonation. If the refractory part of the TOC were also refractory to acid bichromate in the COD test, the ratio of COD to TOC could be expected to drop below the expected ratio of 2.67:1 for carbohydrates and most proteins. Results in all tests show that this ratio (COD:TOC) does, in fact, decrease with increasing ozonation, thus lending credence to the concept of an ozone-refractory class of compounds. These tests also indicate that ozone selectively attacks those compounds which contribute most to oxygen demand. This is of particular importance for maintenance of dissolved oxygen levels in bodies of water into which tertiary effluents will be discharged.

The effects on ozonation rates of preclarification and of the type of coagulant used are shown in Figure 6 (a plot of TOC versus time) and in Figure 7 (a plot of COD versus time). The results obtained for TOC removals were treated in the manner previously explained, and the results are shown in Figure 8 (a plot of non-refractory TOC versus time). The slopes of the lines indicating relative reaction rates are shown in Table IX.

The type of coagulant used had little effect on the efficiency of coagulation, but had a marked effect on the rates of COD removal (see Figure 7); in general, low pH resulted in lower rates. Ozone decomposition in aqueous solution increases rapidly with increased alkalinity[8]; thus, activity of the dissolved ozone in solution is enhanced by higher pH. In these batch tests with excess ozone and effective agitation, the chemical reactions are rate controlling, and the pH effect is not masked by mass transfer effects.

Figure 6 shows that the coagulants remove part of the refractory TOC, thus making a lower final TOC possible. Alum was the most effective coagulant in this respect. Figure 8 and Table IX show that non-refractory TOC removal rates are approximately the same for alum, lime and no coagulant, but significantly lower for alum plus acid.

Thus, the decrease in COD is a primary indicator of the reaction of organics with ozone, and depends directly on the activity of the ozone which in turn depends on the pH. The TOC decreases only if the organic molecules decompose by splitting off carbon dioxide. The rate of this decomposition is reduced only at a pH below 7. The efficiency of ozone consumption was not calculated in this series of tests since expected analytical errors would be great for the excessive quantities of ozone used.

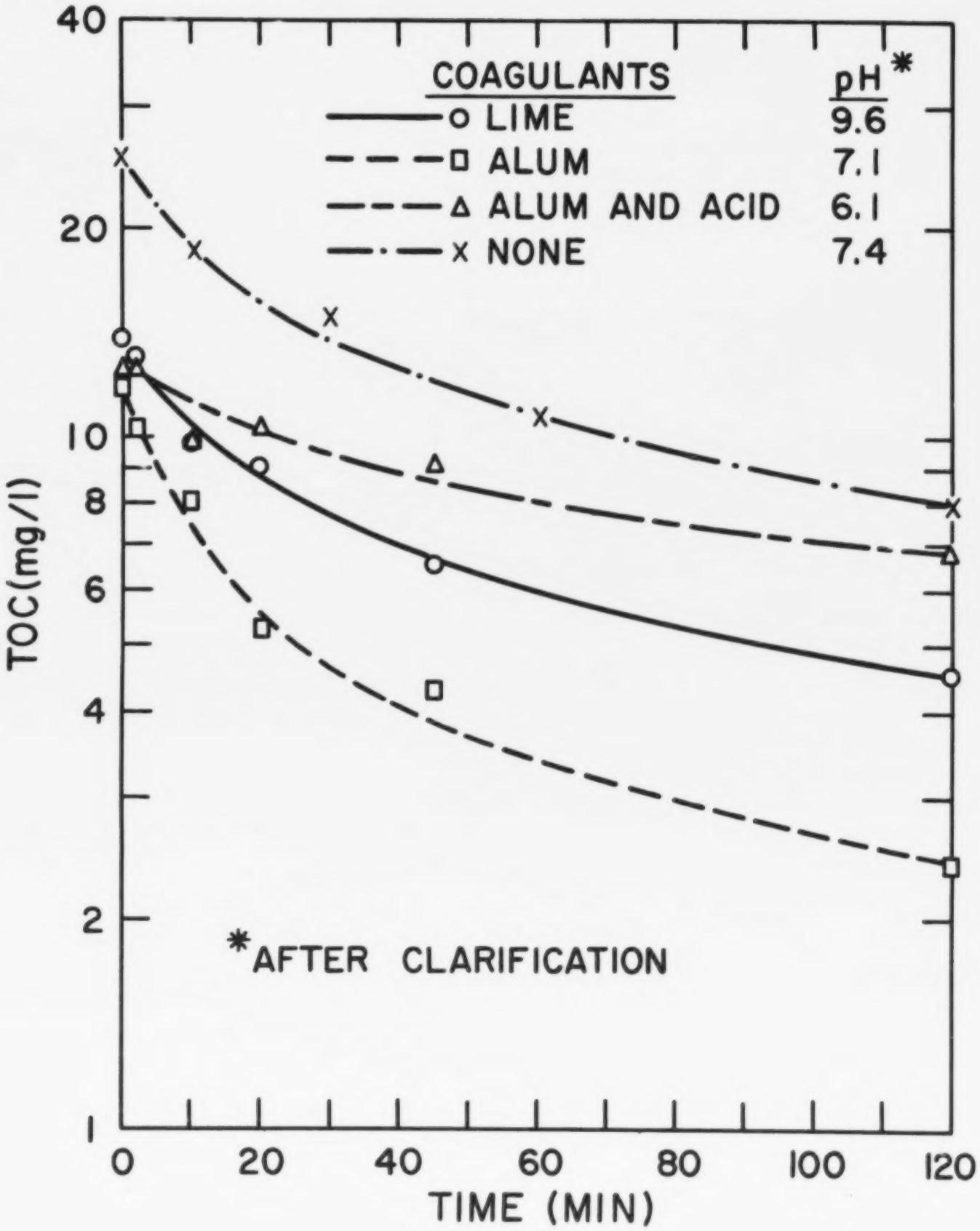

Figure 6. Ozonation in the high-shear batch reactor: effect of clarification on TOC removal with excess ozone.

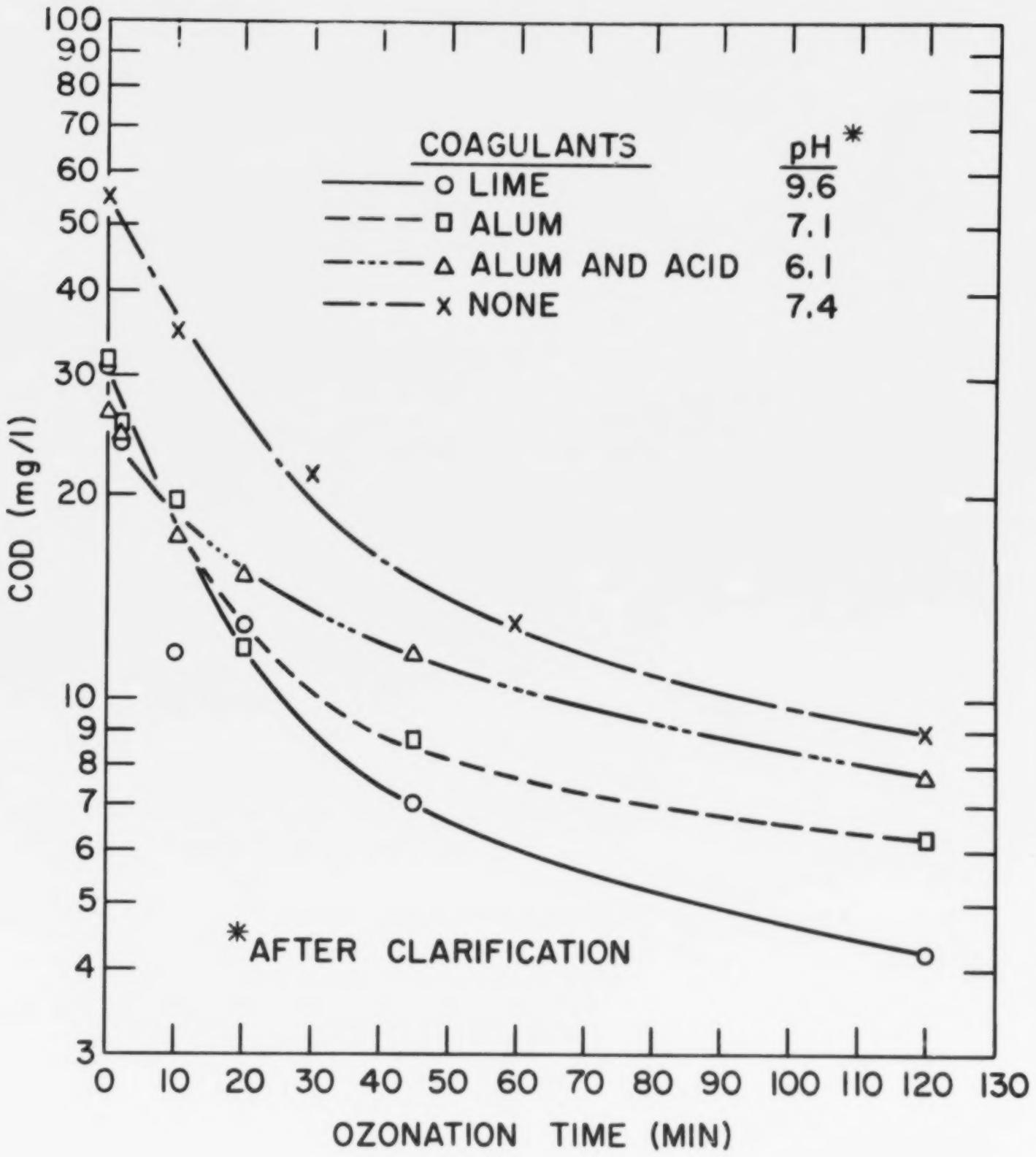

Figure 7. Ozonation in the high-shear batch reactor: effect of clarification on COD removal with excess ozone.

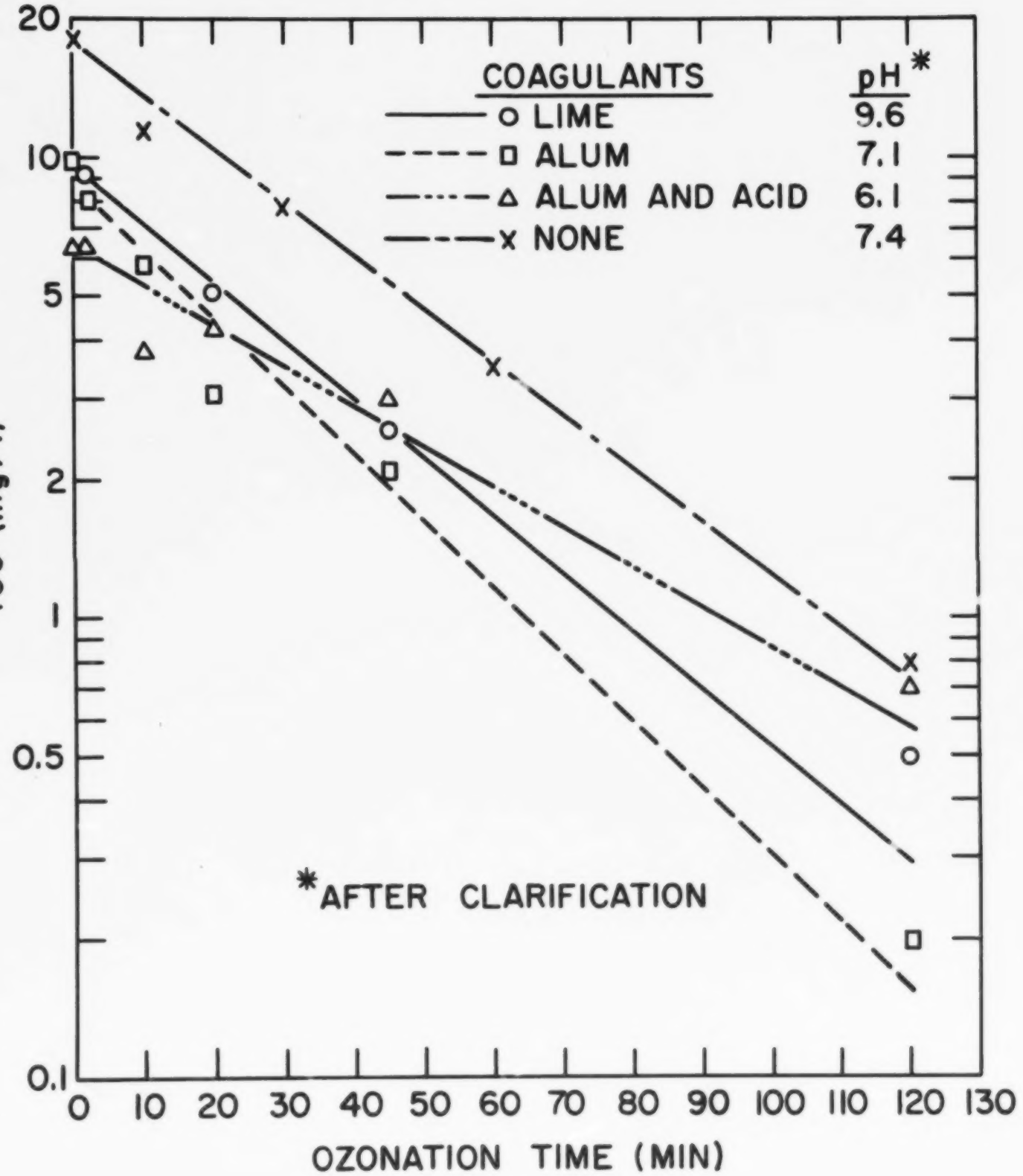

Figure 8. Ozonation in the high-shear batch reactor: effect of clarification on non-refractory TOC removal with batch reactor.

TABLE IX

FIRST-ORDER RATE CONSTANTS FOR NON-REFRACTORY TOC REMOVALS WITH EXCESS OZONE IN THE HIGH-SHEAR BATCH REACTOR

Coagulant	pH After Filter	Rate Constant, min^{-1}
Alum + Acid	6.1	0.020
Alum	7.1	0.034
None	7.4	0.027
Lime	9.6	0.029

The majority of the tests in the batch reactor were conducted with 3.4 wt.% ozone in oxygen (45.2 mg/l). Welsbach data[13] show that ozone production costs are lowest for 1.7 wt.% ozone in oxygen (22.6 mg/l). A series of tests was made to investigate the effect of ozone concentration on the rates of TOC and COD removal. The results in Figure 9 show no rate difference between 3.4 wt.% and 1.7 wt.% ozone. Filtered uncoagulated effluent was used in these tests. Each day for three days, one test with 3.4 wt.% ozone and one with 1.7 wt.% ozone were conducted using a cut of the same effluent. The values plotted are the arithmetic means of the results.

A second series of tests using alum-and-acid-clarified effluent was conducted comparing 1.7 wt.% and 0.8 wt.% ozone. The arithmetic means of the results of this series, shown in Figure 10 (a plot of TOC and COD *versus* time), show no significant differences in reaction rates.

Kilpatrick *et al.*[8], report that light accelerates the decomposition of ozone in aqueous solution. Since their batch tests were conducted in glass equipment in the presence of natural light, there was some question of the applicability of results obtained for design of commercial units wherein light would probably be absent. A series of runs was conducted to study the effect of light. The results in Figure 11 (a plot of TOC and COD *versus* time) showed no difference in reaction rates.

Up to this point, our work on ozone treatment had not proven that reduction in COD to 15 mg/l would bring a corresponding reduction in BOD. Since BOD is the presently used quality criterion for regulating effluent treatment, a knowledge of this relationship is important. Thus, special tests were made for comparing BOD of ozone-treated effluent with COD.

Filtered effluents from Berkeley Heights and Florham Park, New Jersey, were treated for one hour in the high-shear batch reactor with oxygen containing 24 mg ozone/l. Samples were sealed in sterile bottles and sent to the laboratory of the FWPCA pilot plant at Blue Plains, Washington, D.C., where BOD determinations were made. The samples sent to Washington were not stabilized with acid, while those used for the COD analyses had the usual acid addition.

Table X summarizes the results for these analyses. With both effluents, the ozone-treated material had a low BOD of about 3 mg/l. The filtered effluent (11-20-1) from the activated sludge plant of Florham Park, had dropped to a rather low BOD (5 mg/l). The oxygen content of this effluent was probably high enough to continue the BOD removal in transit.

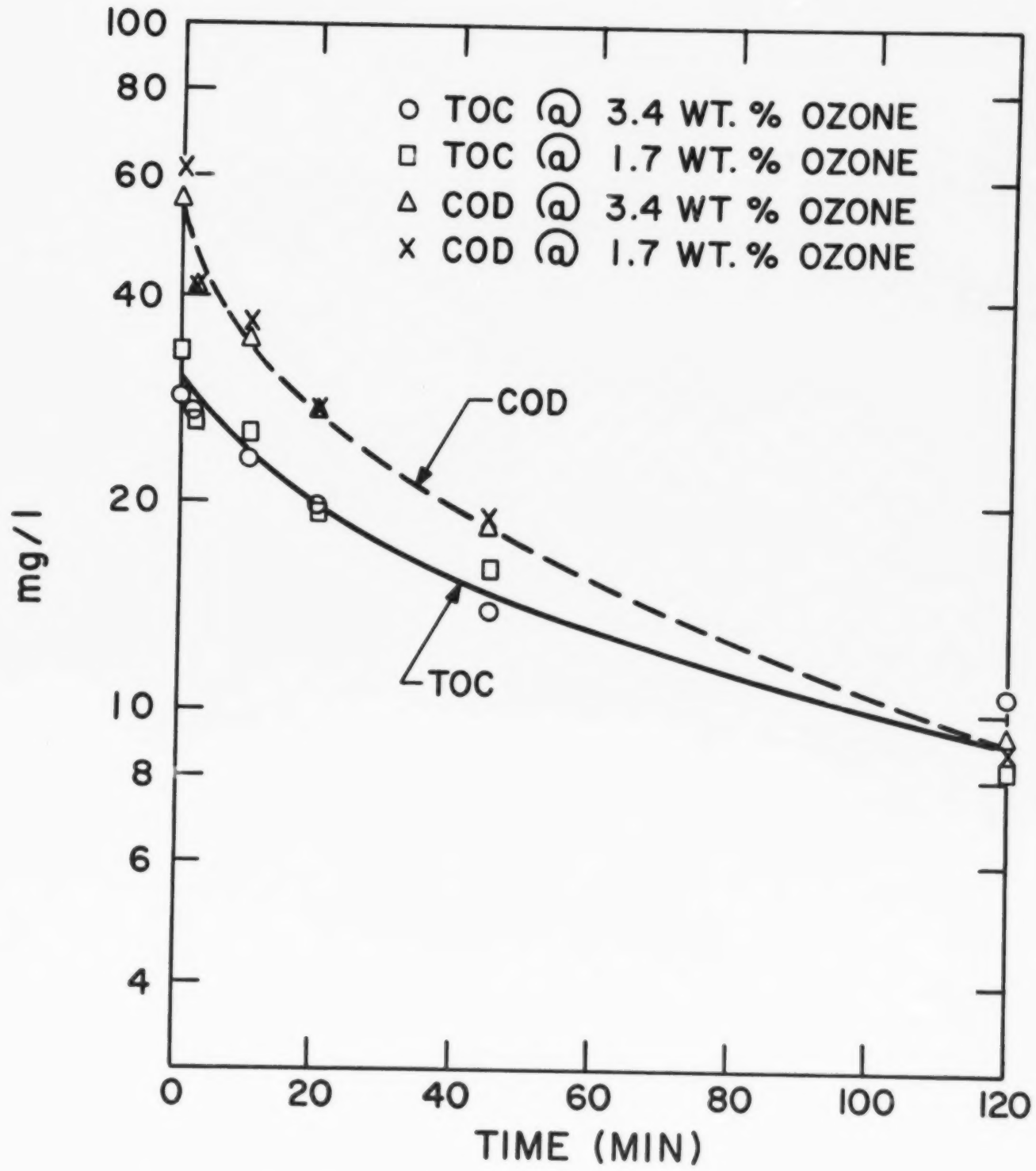

Figure 9. Ozonation in the high-shear batch reactor: effect of ozone concentration on TOC and COD removals with filtered, unclarified effluent and with excess ozone.

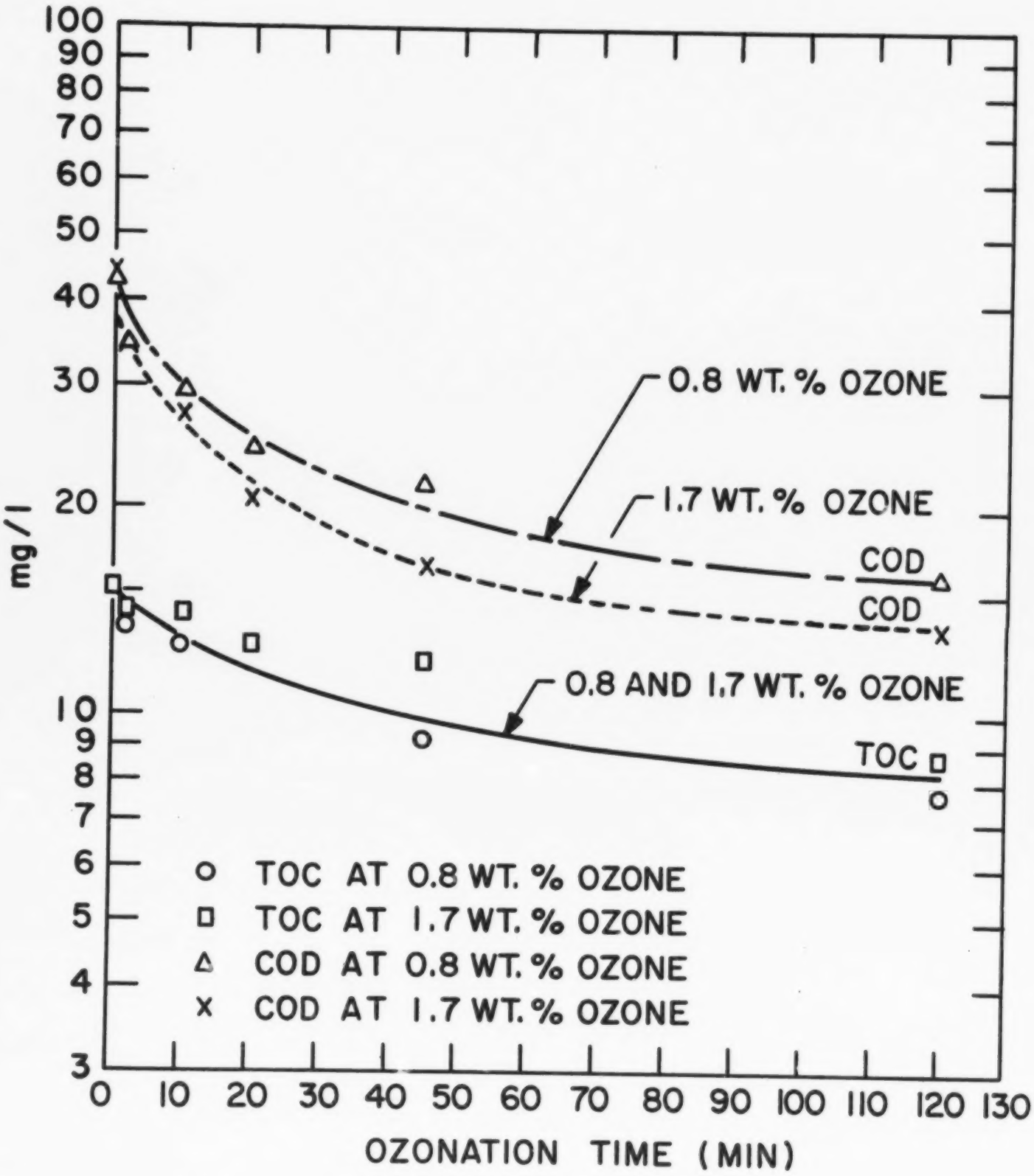

Figure 10. Ozonation in the high-shear batch reactor: effect of ozone concentration on TOC and COD removals with clarified effluent and with excess ozone.

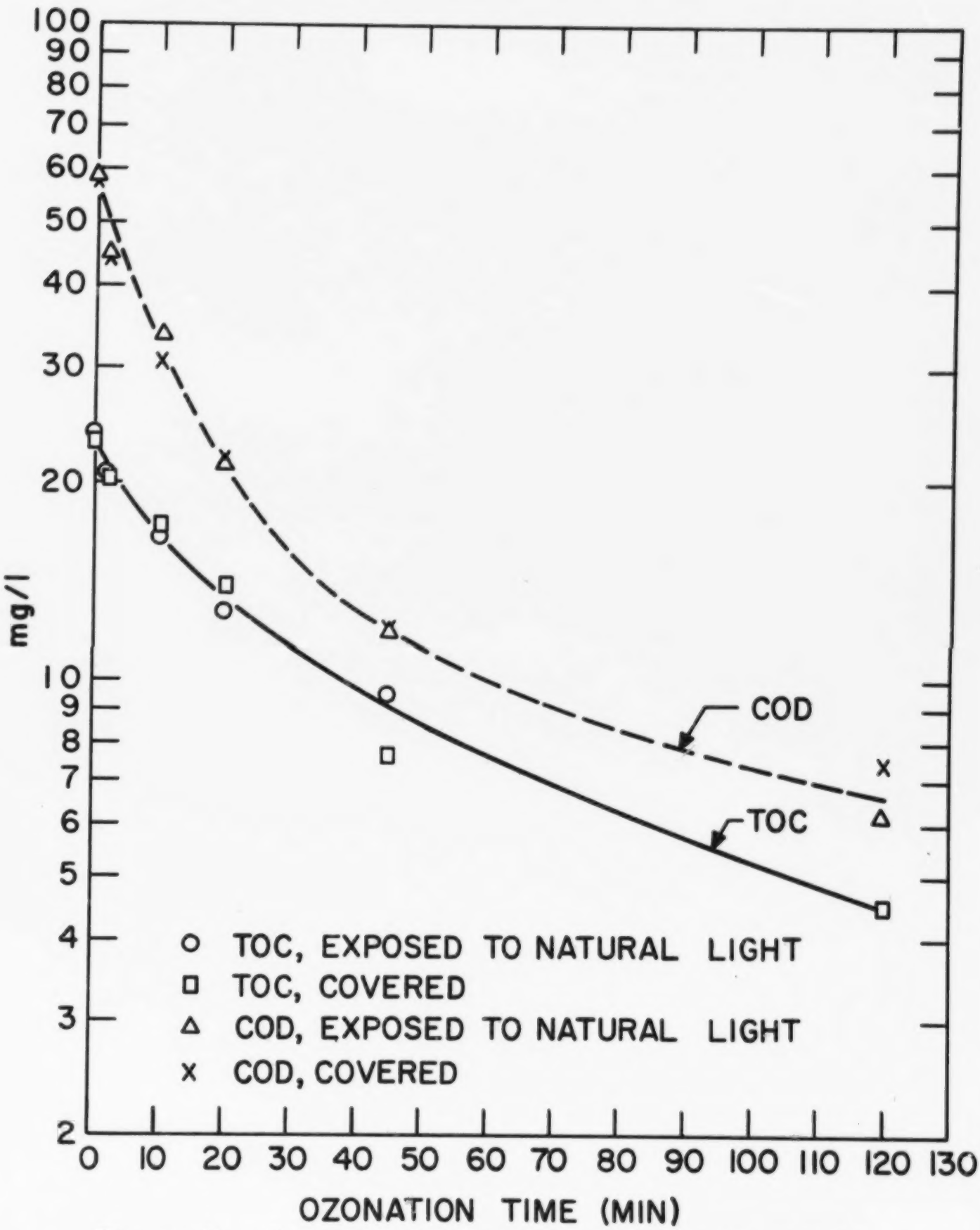

Figure 11. Ozonation in the high-shear batch reactor: effect of exposure to natural light on TOC and COD removals with excess ozone in the high-shear batch reactor.

TABLE X

BIOCHEMICAL OXYGEN DEMAND OF EFFLUENTS
TREATED 60 MINUTES WITH OZONE IN THE
HIGH-SHEAR BATCH REACTOR

Berkeley Heights Effluent, Samples 11-14-0 through 11-14-4
Florham Park Effluent, Samples 11-20-0 through 11-20-4

Sample Number	Source	Turbidity, J.T.U.	COD, mg/l	BOD, mg/l
11-14-0	Original Effluent	30	63	51
11-14-1	Filtered Effluent #1	15	44	36
11-14-2	Ozone Treated #1	2	16	4
11-14-3	Filtered Effluent #2	15	44	36
11-14-4	Ozone Treated #2	2	16	3
11-20-0	Original Effluent	23	61	-
11-20-1	Filtered Effluent #1	9	34	5
11-20-2	Ozone Treated #1	2	13	3
11-20-3	Filtered Effluent #2	12	36	-
11-20-4	Ozone Treated #2	2	13	2

SIMULATION OF A SIX-STAGE COCURRENT CONTACTING SYSTEM

High ozone-utilization efficiency is the key to economic water treatment. Ozone is most efficiently used when it is consumed quickly. By cocurrent contacting, ozone and organic matter are brought together at their highest concentrations, thus obtaining the maximum, initial, reaction-driving force and consuming the bulk of the ozone in useful reaction before its spontaneous decomposition can occur. High-shear contacting of entering effluent with entering gas in an injector aids rapid transfer of ozone from the gaseous to the aqueous phase.

The reaction between dissolved ozone and many of the organic compounds to be removed is slow. Consequently, all of the ozone must not be introduced at one time. The use of several stages is required. The experiments described below simulated a six-stage cocurrent reaction system. Because ozone has a half-life in water of about 20 minutes, a 10-minute residence time per stage was selected. About an hour is needed to reduce the COD from about 35 to 15 mg/l. Therefore, six stages were used.

Equipment and Procedures

The 18-foot column was modified as shown in Figure 12 to simulate multistage contacting. Ozone in oxygen was mixed with effluent in an injector. The dispersed mixture descended a 20-foot dissolving tube and entered the bottom of the column. Both the gas and liquid then flowed upward through the column packing, and the liquid was returned through an overflow siphon at the top to the suction of the recycle pump. The liquid flow rate was adjusted to provide for a recycle time of 10 minutes, representing the performance of one stage. In one hour, a six-stage system was simulated. The holdup time for the gas was about one minute.

The recycle pump was a stainless steel, positive displacement, sanitary pump with a variable-speed drive. A by-pass valve made fine adjustment of the flow possible.

The vertical 20-foot dissolving tube gave a contact time for intensive gas-liquid contacting of about 6 seconds. The increasing hydrostatic pressure exerted, as the mixture flows down, improves ozone transfer from the gaseous to the liquid phase in the mixture. This principle is also used in the so-called Otto process for ozonizing drinking water. The Otto process, however, is limited to one stage since much less ozone is needed to sterilize drinking water.

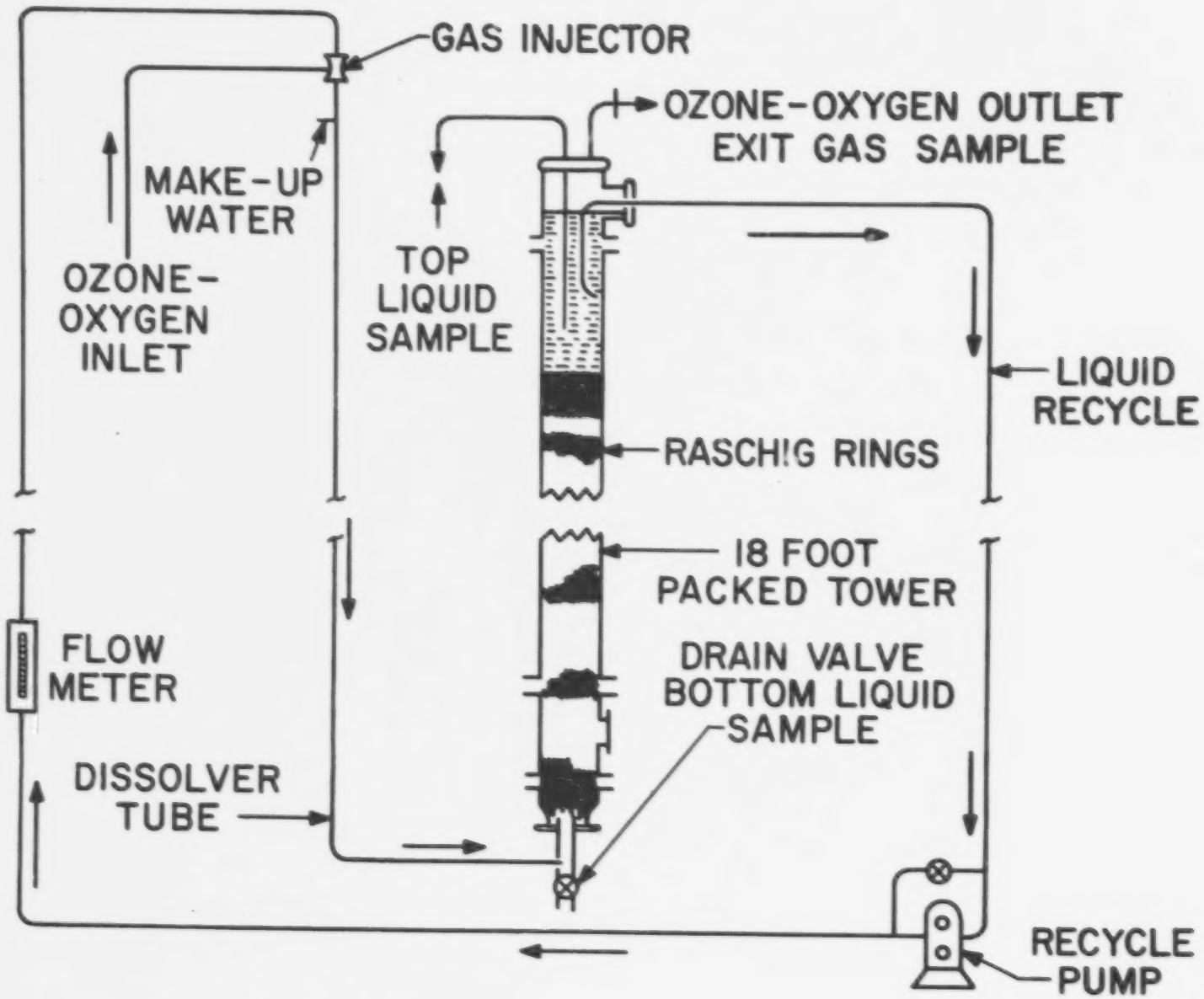

Figure 12. Schematic diagram of the simulated multistage cocurrent contactor.

Normally, liquid samples were taken for analyses at 10, 20, 40, and 60 minutes after the start of the run. Outgoing gas samples were taken at 2, 30, and 50 minutes. This timing was used to avoid taking gas samples while the system was being disturbed by the liquid sampling. Introduction of untreated effluent for make-up, after sampling, caused an increase in the TOC and COD. To check this effect on the TOC and COD obtained after 60 minutes, run 117 was made without taking liquid samples during the run so that no make-up with untreated effluent was required.

The ozone input could be adjusted at various stages of the experimental run to match the ozone demand of the effluent. Thus, the effect of excesses and deficiencies of ozone at various stages could be analyzed.

The ozone generator could produce mixtures ranging from 21 to 48 mg/l ozone in oxygen. To obtain lower ozone concentrations, oxygen from a separate cylinder was passed through a flow meter and was then mixed with the stream from the ozonizer. The settings of the ozonizer and flow controls were governed by ozone analyses of the mixed stream.

Results and Discussion

Results from representative runs are shown in Tables XI and XII. All of the effluents used in these simulation tests were coagulated, settled, and filtered.

The COD/ozone efficiency indices of the first stages of all the experiments with this system, except the one with the highest pH, were over 100%. The more-active organic compounds in the effluent apparently used more than one oxygen atom per ozone molecule. This phenomenon was also reported recently by Koppe and Giebler[13].

Runs 109 and 111 were made at a low ozone concentration of 10.6 mg/l and a constant gas flow rate throughout the run. The COD/ozone efficiency indices decreased very rapidly from about 200% in the first stage, to about 110% in the second stage, and to 81% and less in the last three stages. This reflects that a deficiency of ozone was fed to the first and the second stages, while an excess of ozone went to the third and subsequent stages.

For runs 113 and 115, the amount of ozone fed to the first two stages was somewhat more than doubled by increasing the ozone concentration to 22.6 mg/l. After 25 minutes, the gas flow rate was halved. In these runs, the COD/ozone efficiency indices were above 100% only in the first stage.

TABLE XI

SIMULATION OF SIX-STAGE COCURRENT OZONATION OF BERKELEY HEIGHTS EFFLUENTS:
OZONE ANALYSES

Run No.	Coagulant, mg/l	pH in the Column	OZONE CONCENTRATIONS							
			Gas In, mg/l	Gas Out, mg/l		Liquid* at Bottom, mg/l at		Liquid* at Top, mg/l at	
				10 Min	60 Min	10 Min	60 Min	10 Min	60 Min
109	Lime-132	8.2	10.6	1.1	5.0	3.0	3.5	1.0	1.0
111	Alum-110 +H_2SO_4-63	6.6	10.6	5.0	5.3	4.7	5.8	1.9	2.5
127	Lime-396	9.0	22.6	0.1	0.0	3.9	0.0	0.6	0.0
113	Lime-132	8.5	22.6	1.3	2.1	12.0	12.0	2.0	2.6
115	Alum-132	7.8	22.6	5.6	8.0	12.0	12.0	4.2	4.0
117	Alum-132	7.8	22.6	**	10.6	**	10.0	**	5.7
123	Alum-110 +H_2SO_4-85	6.2	22.6	5.7	4.9	15.0	6.0	6.0	2.0

*Saturated aqueous solution in contact with 1 atm gas containing 10.6 mg O_3/l = 4.6 mg O_3/l
Saturated aqueous solution in contact with 1 atm gas containing 22.6 mg O_3/l = 9.7 mg O_3/l

**No samples taken until end of run

TABLE XII

SIMULATION OF SIX-STAGE COCURRENT OZONATION OF BERKELEY HEIGHTS EFFLUENTS:
TOC & COD REMOVALS

Run No.*	pH	COD of Feed, mg/l	STAGE NUMBER 1: COD out, mg/l	1: O_3 in, mg	1: COD/Ozone Efficiency Index, %	2: COD out, mg/l	2: O_3 in, mg	2: COD/Ozone Efficiency Index, %	3: COD out, mg/l	3: O_3 in, mg	3: COD/Ozone Efficiency Index, %	4: COD out, mg/l	4: O_3 in, mg	4: COD/Ozone Efficiency Index, %	5: COD out, mg/l	5: O_3 in, mg	5: COD/Ozone Efficiency Index, %	6: COD out, mg/l	6: O_3 in, mg	6: COD/Ozone Efficiency Index, %
109	8.2	36	27	400	214	23	400	108	22	400	40	21	400	27	20	400	8	20	400	-
111	6.6	36	27	400	190	23	400	108	20	400	81	18	400	53	17	400	25	17	400	-
127	9.0	30	22	989	69	17	791	68	16	395	27	18	395	-	18	395	-	18	395	-
113	8.5	43	31	791	143	24	791	96	21	593	55	20	395	27	19	395	13	19	395	-
115	7.8	5	24	791	124	20	791	62	18	593	27	17	395	27	16	395	14	16	395	14
123	6.2	41	27	989	119	23	791	68	20	395	82	18	395	55	16	395	41	15	395	27

Run No.*	Coagulant: $Ca(OH)_2$, mg/l	Coagulant: Alum, mg/l	Coagulant: H_2SO_4, mg/l	pH: Raw Effluent	pH: After Filter	pH: Ozone Treated	Raw Effluent: TOC, mg/l	Raw Effluent: COD, mg/l	Raw Effluent: Turbidity, JTU	After Filter: TOC, mg/l	After Filter: COD, mg/l	After Filter: Turbidity, JTU	After 60 min. O_3 Treatment: TOC, mg/l	After 60 min. O_3 Treatment: COD, mg/l	After 60 min. O_3 Treatment: Turbidity, JTU	Overall Efficiency Indices, %: TOC/O_3	Overall Efficiency Indices, %: COD/O_3
109	132	-	-	7.2	8.2	8.2	28	75	39	17	36	8	10	20	2	89	76
111	-	110	63	7.4	5.6	6.6	29	91	49	11	36	9	9	17	3	25	90
127	396	-	-	7.2	10.8	9.0	30	89	60	11	30	8	9	18	2	18	41
113	132	-	-	7.3	8.7	8.5	24	70	39	15	43	8	8	19	3	64	78
115	-	132	-	7.5	6.8	7.8	21	83	39	14	35	8	11	16	2	27	61
117**	-	132	-	7.5	6.8	7.8	42	98	46	12	32	6	9	13	3	25	58
123	-	110	85	7.2	5.3	6.2	31	96	39	22	41	10	11	15	9	98	88

*Effluent feed rate = 9 gal./hr. Initial charge = 9 gal., plus 1 gal. to compensate for samples (except in Run 117)
**Samples taken only at 60 min.

In runs 123 and 127, the ozone feed rate was changed twice: first at 10 minutes, (from 98.9 mg O_3/min to 79.1 mg O_3/min) and again at 20 minutes, (from 79.1 mg O_3/min to 39.5 mg O_3/min). The ratio of the ozone feed rates for the first/second/subsequent stages was 15/12/6. This brought the ozone feed closer to the expected ozone demand in the first three stages. In run 123, this resulted in a gain in overall efficiency. In run 127, the COD of the feed was considerably lower which, in combination with the high dosage of lime coagulant, reduced the overall COD/ozone efficiency index to only 41%. The relatively good performance in run 113, using a lower lime dosage for clarification, followed a thorough cleaning of the system with inorganic alkaline cleaners. After cleaning, the first rinse was neutralized with nitric acid to pH = 7. This was followed by several water rinses.

Table XI gives the ozone concentrations in the gas and liquid phases at the beginning and end of each run. The data show that ozone decomposed more readily in run 127 where the effluent had a high pH as a result of coagulation with a large dose of lime. This increased ozone decomposition was accompanied by a loss in oxidation efficiency. A time-delay effect was noticed. Decomposition became more severe with passage of time during the run and was more sensitive to pH in these experiments than in the countercurrent experiments or in the experiments with the batch reactor. The ozone-water mixture passed down a long, small-diameter tube from the injector. In this tube, and on the packing of the column, ozone contacted a large solid surface in proportion to the volume of the system. At a high pH, alkaline deposits that catalyze ozone decomposition are probably formed. A small apparatus of this type should be more sensitive to surface-catalyzed ozone decomposition than full-scale equipment with a lower surface-to-volume ratio.

A semi-log plot of some of the COD values against time is shown in Figure 13. The form of these curves is similar to those obtained for the batch reactors. They are not corrected for the addition of untreated effluent to make up for the volume of the samples taken during the runs. This raised the TOC and COD above their proper values. Run 117 was made to check the amount of this increase by taking samples only at the end of the run so that nothing was added to the original charge. The average final COD was 13 mg/l, 3 mg/l lower than in the comparable run 115 with normal sampling. TOC was 2 mg/l lower.

For scale-up, alum or alum-acid coagulation is preferred, unless a means can be found to prevent the formation of scale deposits when using lime.

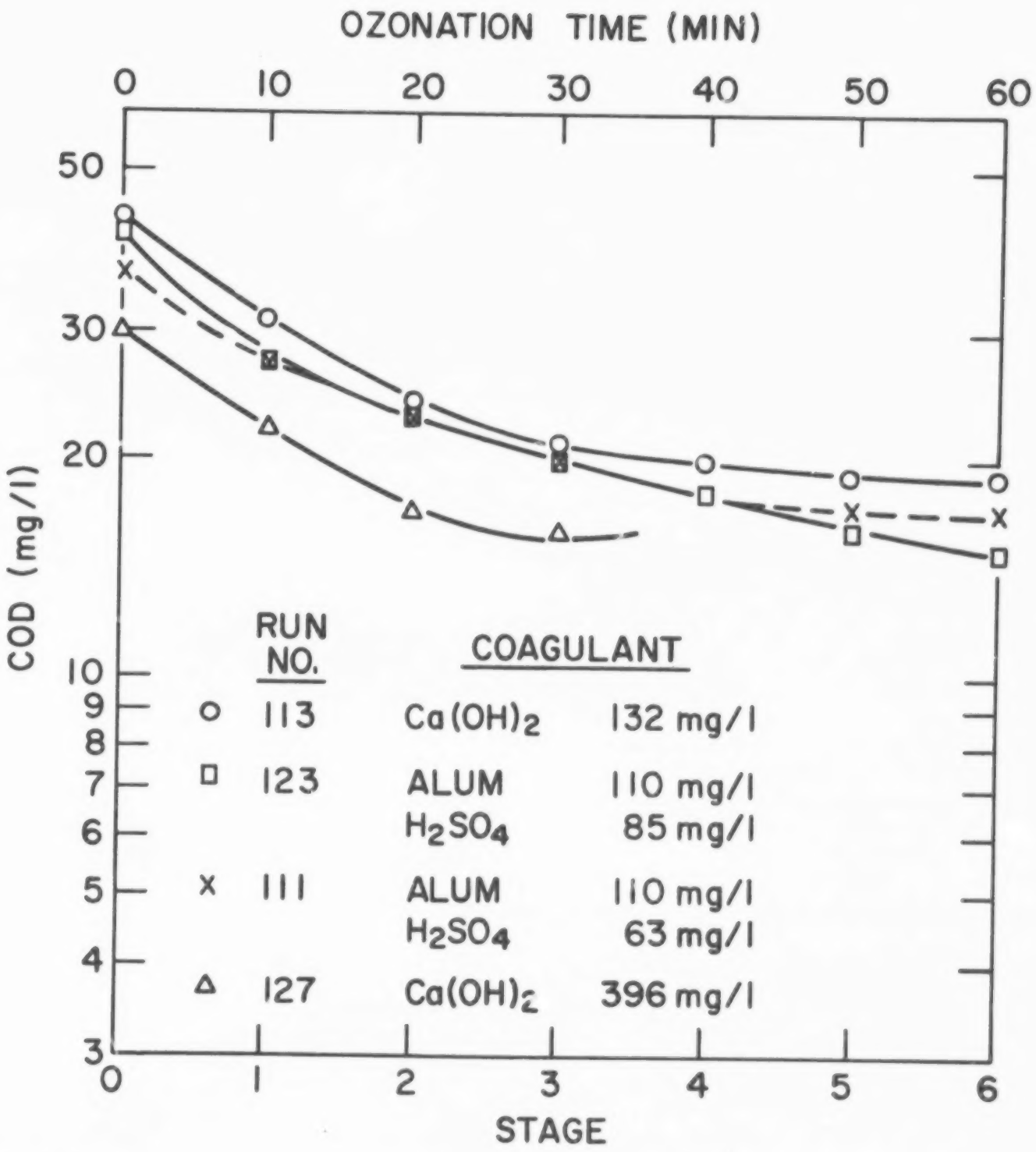

Figure 13. COD removals in the simulated six-stage cocurrent system.

DESIGN CONCEPTS AND CRITERIA

Ozone Supply

The instability of ozone prevents its sale as a "packaged" commodity; therefore, it has to be produced at the use point. Many methods are available for the production of ozone, the most common being silent electric discharge in oxygen or air, photochemical conversion of oxygen or air, and electrolysis of sulfuric acid. The photochemical method of ozone production is used where small quantities in very low concentrations are required. For large-scale production, the silent-electric-discharge method is the only practical and economical method.

The choice of whether to use air or pure oxygen as feed to a silent-electric-discharge ozonator is essentially a question of economics. For a given ozonator with a constant power input, approximately twice as much ozone is generated from oxygen as from air[14]. Thus, per lb. of ozone produced, capital and electric power requirements would be considerably less with oxygen usage. Against this saving must be charged the cost for oxygen. For large ozone installations using oxygen, the reuse of unconsumed oxygen becomes an economic necessity. In general, for large ozone usage, the most economical system uses oxygen with recycle. An additional benefit of the recycle system would be the elimination of air pollution problems caused by the discharge of spent gas containing unconsumed ozone.

A recycle system in a waste-water ozonation plant requires an oxygen purification system. The recycled oxygen has a high humidity and contains carbon dioxide (from the oxidation of organics), nitrogen, and possibly hydrocarbons desorbed from the secondary effluent through which the oxygen has passed.

Studies conducted into the effects of various gaseous contaminants on yield of ozone per unit of electrical energy expended have shown that even minute quantities of water can cause drastic drops in production efficiency[15,16]. The presence of other contaminants have varying effects; i.e., hydrogen behaves similarly to water, whereas carbon dioxide, argon, and hydrocarbons decrease efficiency only gradually. The presence of nitrogen or carbon monoxide increases efficiency when present in concentration up to 10%, but causes a decrease in efficiency at greater concentrations. The recommended practice is to supply the ozonator with oxygen or air dried to a dew point of -60°C and with an organic content of less than 15 ppm by volume.

Process Design

The optimum treatment of secondary effluent with ozone, as evolved from our experimental program, consists of a pretreatment by clarification, if required, followed by deaeration and a stagewise contacting with ozone for short periods. The vessel of each contacting stage should provide the needed residence time for the reaction of ozone with organics.

The requirement for pretreatment will depend primarily on the quality of effluent from the secondary plant and on the required quality of the ozonated water. For each case, an economic comparison between pretreatment costs and the incremental increases in ozone-treatment costs will determine the method to be used. Our studies have indicated that pretreatment is preferred for effluents having COD values above 40 mg/l.

Operating costs of ozone treatment reflect two major items of expense: plant amortization and power costs. The oxygen requirement is relatively fixed and is determined by COD removal achieved and oxygen dissolved in the outgoing effluent. Labor costs and maintenance are quite low. The key to economic water treatment is high ozone-utilization efficiency. The design and operational modes of the plant must be directed foremost to this problem.

The continuous and spontaneous decomposition of ozone in water requires that the ozone react with organics as quickly as possible in order to achieve highest utilization efficiency. Cocurrent contacting of ozone and effluent brings ozone and organics together at their highest concentrations, resulting in the maximum driving force for the useful consumption of ozone.

The chemical reaction between dissolved ozone and the organics in the effluent is a time-dependent process. Experimental evidence has shown that about one hour is required to reduce the COD content to an acceptable level of approximately 15 mg/l from an intake value of 35-40 mg/l; whereas, the half-life of ozone in water is about 20 minutes. Consequently, all the ozone must not be introduced at one time; staging is required. Ten minutes has been selected as a reasonable residence time per stage. The approximate removal of COD per stage that occurred in our experiments is shown in Table XIII.

For maximum ozone utilization, the ozone supplied,per stage, should be equivalent to the amount that can be usefully consumed. This latter amount depends on the COD levels and can be evaluated with the high-shear batch reactor. Table XIII shows how the ozone supply per stage should be reduced as a function of stage position. Thus, the first stage should receive more ozone than the second, etc.

Our experiments showed that overall rates in the two-phase ozonation systems are dependent on the resistances both to mass transfer and to chemical reaction with ozone. A significant

TABLE XIII

SIX-STAGE COCURRENT OZONATION:

COD REMOVAL PER STAGE

Stage (10 min. per Stage)	Percent of Total COD Removal	
	High-Shear Batch Reactor (Alum-Acid Clarification Runs)	Simulated Six-Stage Contactor (Run 123)
1	51	52
2	19	16
3	12	12
4	9	8
5	6	8
6	3	4
Total	100	100

decrease in either one of these resistances would increase overall rates significantly. High-shear contacting of effluent with ozone in injectors achieved high mass-transfer rates and appeared more economical than turbine agitation. Thus, the use of injectors has been specified for the proposed plant design.

The holdup tanks incorporated in the system have a twofold function: (1) as a secondary absorber for ozone from the gas that was not transferred in the injector or the dissolver tube; (2) as a time delay for the effluent to assure that the dissolved ozone is consumed, thus giving maximum drive for mass transfer of ozone in the next stage.

The pH of the solution affects the rates of spontaneous ozone decomposition and of reaction of ozone with organics. The higher the pH, the greater the rates. For optimum economic operation, the ozonation rates must be balanced against the utilization efficiency of ozone. Our experiments indicate that a slightly acid pH (pH 6.0 to 7.0) is optimum for multistage cocurrent ozonation.

PLANT DESCRIPTION

A schematic flowsheet of the proposed ozone-treatment plant for waste water is shown in Figure 14. Secondary effluent, either direct from the secondary treatment plant or from a clarifier, is pumped via a deaerator to the injector-type contactor of the first stage. Oxygen containing ozone is simultaneously fed into the injector to effect complete mixing of the two phases and to induce high-shear contact for improved mass transfer. The two-phase mixture is discharged at the bottom of the first-stage holdup tank. The liquid from the top of the tank is used as a feed for the next stage. The ozone-depleted oxygen stream from the tower is combined with gas streams from the other stages and is recycled. The gas feed to all contactors is parallel and is proportioned according to requirements. In general, the quantity of ozone fed diminishes between each successive contactor; thus, the first-stage contactor receives a greater quantity of ozone than the next stage, etc. As explained before, the liquid from the last-stage contactor is discharged without any further treatment.

The recycled, oxygen, gas stream is compressed to about 10-15 psig (the pressure required to overcome losses in lines and equipment), is cooled to 35°F by a direct-contact chilled-water spray tower, and is passed through regenerative gas dryers (molecular sieve, alumina or silica gel) to dry the oxygen to the required dew point of -60°F. The dried gas is then sent to the bank of ozone generators to produce ozone at 1.7 wt.% concentration (22.6 mg/l). Makeup oxygen, as required, is introduced into the recycle stream between the dryers and the ozone generators.

The build-up of nitrogen and carbon dioxide in the recycle gas stream has to be controlled. It was estimated that removal of dissolved nitrogen in the secondary effluent feed by vacuum deaeration would eliminate the need of a purge. Vacuum deaeration could be carried out in a relatively simple vessel in which a pressure of 2 psia is maintained by a small vacuum pump. The expected oxygen consumption is given in Table XIV. An extra allowance of 0.12 lb. of oxygen per 1000 gal. was made for occasional purge requirements and leakage.

Most of the carbon dioxide produced in ozone treatment should be discharged from the system as dissolved gas in the liquid effluent. Further control of carbon dioxide levels in the recycle stream can be effected by adsorption in the dryers, if required.

The gas exiting from the contactors is expected to contain residual ozone in quantities estimated at 10 to 25% of that in the incoming feed. Commercial operation of ozonation systems[17] has shown that a portion of the residual ozone would pass through

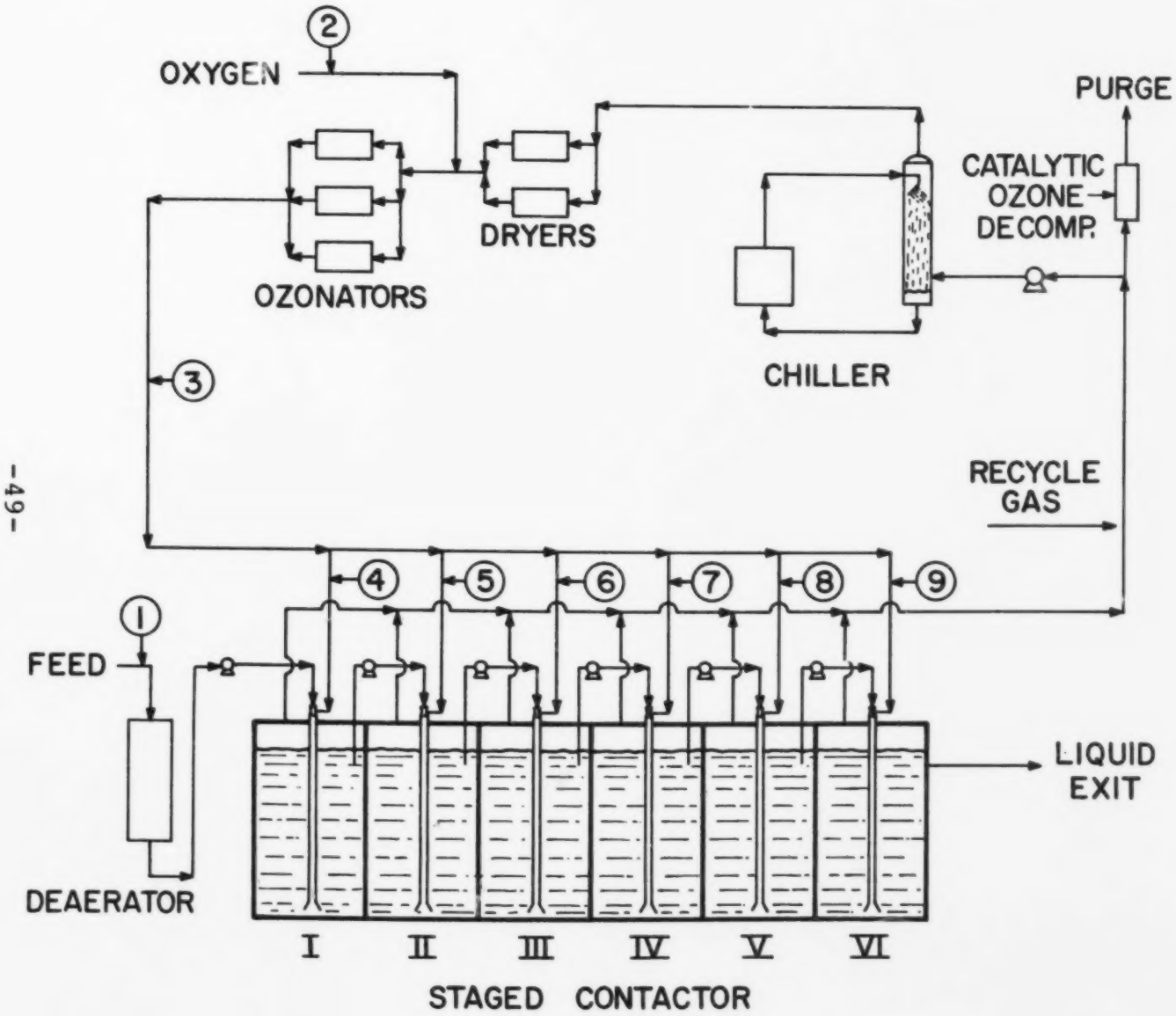

Figure 14. Ozone treatment plant

FLOW RATES FOR 10 MGD PLANT

(1) EFFLUENT = 6,940 GPM

(2) OXYGEN MAKEUP = 6,340 lb/day

(3) OZONE GAS = 309 SCFM FEED (26 lb/min @ 1.7 wt.% OZONE)

GAS FEED TO STAGES

LINE NO	FLOW SCFM	% TOTAL GAS
4	157	51
5	59	19
6	37	12
7	28	9
8	19	6
9	9	3

TABLE XIV

OXYGEN CONSUMPTION IN LB. PER 1000 GAL. EFFLUENT TREATED

	Vacuum Deaeration
Oxygen Absorbed by Effluent	0.35
Oxygen Consumed in Lowering COD	0.17
Oxygen Lost by Purge and Leakage	0.12
Total	0.64

recycle systems unaffected and would be available again at the contactor. The proportion passing through the proposed recycle system is unknown; and in the estimate, possible recycle ozone has not been taken into account.

Alternate recovery methods for the residual ozone are possible. Scrubbing of the exit gases by fresh effluent prior to recycle is an obvious example. However, because of the low ozone concentration in the exit gases, effective utilization or alternate recovery of residual ozone would entail rather elaborate and expensive mass transfer equipment. Savings resulting from recovery would appear to be rather small compared to total costs; therefore, no attempt was made to estimate these savings. We realize that an in-depth study could reveal other potential savings, and various recovery methods or destruction methods must be studied for any commercial endeavor.

The holdup tanks were designed for a 10-minute retention time per stage. As explained in the previous section, one of the functions of each holdup tank is to act as a secondary absorber for ozone in the gas stream. In order to achieve effective gas scrubbing, gas distribution within the tank should be uniform. The cross-sectional area of the tank should be maintained within reasonable limits. A height-to-width ratio per injector of 2:1 was chosen as a reasonable value. Thus, an injector placed in a tank with an 18-foot water depth will cover an area approximately 9 feet wide. The 10-million GPD contactor system, as shown in Figure 15, consists of six chambers, each of which is 63 feet long x 18 feet deep. These chambers represent the six stages. Each stage has seven injectors fed by one pump. The area covered by each injector is 9 feet wide or 81 square feet.

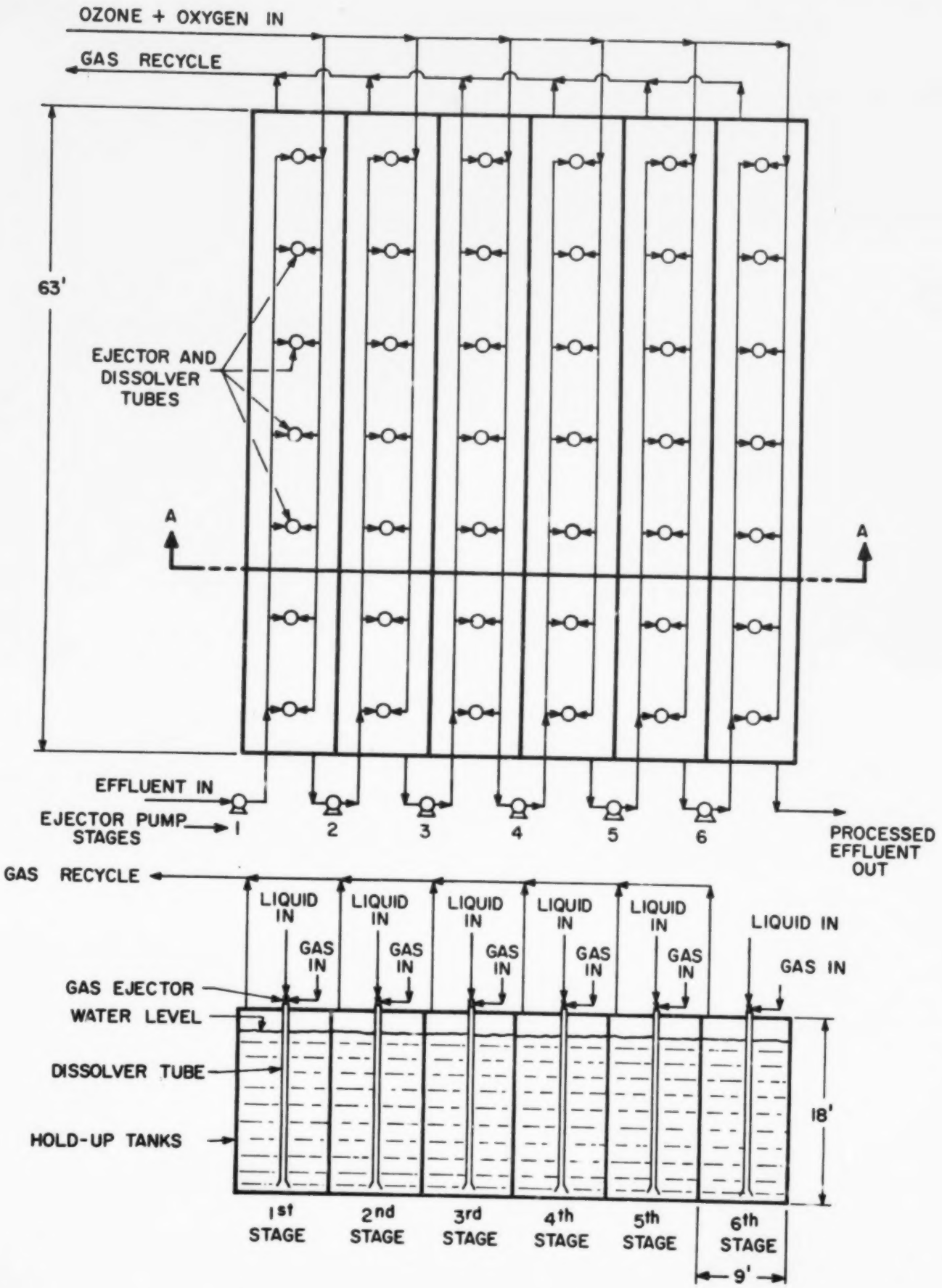

Figure 15. Schematic representation of a 10-million gpd plant for ozone treatment of secondary effluent

CAPITAL COST ESTIMATE

Capital cost requirements for ozone-treatment plants of three sizes (1-, 10-, and 100-million GPD) were estimated and are presented in Table XV. The estimates are made for a COD decrease from 35 to 15 mg/l, and an overall ozone-utilization efficiency (COD/ozone efficiency index) of 80%. The plant design is based on existing means of ozone manufacture and on a direct scale-up of our laboratory findings.

Most existing secondary-treatment plants probably do not discharge effluent with a COD content as low as 35 mg/l. Higher COD loadings up to 250 mg/l are common. Tertiary treatment of these high-COD effluents by ozone, alone, would be too expensive. Pretreatment by chemical coagulation and filtration, or in some cases by filtration alone, can result in lower overall costs for the tertiary treatment process. The decision for or against this pretreatment would be based on a comparison of the incremental cost increase of the ozone treatment plant *versus* the cost of a pretreatment plant. The decision must be made on a specific-case basis for existing, and proposed, secondary-treatment plants.

The average capital requirements for chemical clarification plants of 1-, 10-, and 100-million GPD are shown in Table XVI.

The estimates of Tables XV and XVI are to be added to the cost of existing secondary-treatment plants; thus, all further treatment costs must be borne by the tertiary treatment plant. Two extreme cases were considered: In the first case, the effluent requires no pretreatment; in the second case, extensive chemical clarification is required. In actual practice, other possibilities could be considered; for instance, an incremental increase in the secondary treatment facility to eliminate, or appreciably reduce, the pretreatment requirement. For new facilities, where it is anticipated that tertiary treatment will be required, design and operation should be based on a total-facility concept for minimum costs. For instance, incremental increases in secondary treatment might eliminate tertiary pretreatment requirements; or conversely, incremental increases in pretreatment (coagulation, filtration) of primary effluent could totally eliminate the need for secondary treatment, as now practiced. The study of all these possibilities and their ramifications is beyond the scope of this program; hence, the simpler case of tertiary treatment costs, as an added-on feature to an existing facility, is presented.

It should be noted that the need for pretreatment prior to a tertiary treatment of waste water is not unique with the ozonation method. The study by Bishop *et al.*[19] and the experience at Lake Tahoe[20] have shown that pretreatment is sometimes required when activated carbon is used for tertiary treatment. The quality requirements of effluent feed for either ozone or activated carbon treatment are essentially equal.

TABLE XV

CAPITAL COST ESTIMATES FOR OZONE-TREATMENT PLANTS

Cost Item	Capital Cost Per Item versus Plant Size, $		
	1-Million GPD	10-Million GPD	100-Million GPD
1. Ozone generators (1)	50,100	330,000	2,300,000
2. Recycle system (2)	39,400	160,000	638,000
3. Contactor (3)	31,300	207,000	1,635,000
4. Piping and pumps	26,500	127,000	1,260,000
5. Facilities & buildings	16,500	65,400	362,000
6. Vacuum deaeration system	4,200	7,500	22,000
Subtotal	168,000	896,900	6,217,000
7. Contingency and profit at 20%	33,600	179,400	1,243,000
8. Total	201,600	1,076,300	7,460,000
9. Total in round figures	202,000	1,080,000	7,460,000

(1) Cost based on data supplied by the Welsbach Corporation
(2) Recycle system includes compressor, water chiller, and chiller tower.
(3) Contactor includes injectors, dissolver tubes and hold-up tanks.

TABLE XVI

CAPITAL COSTS FOR CHEMICAL CLARIFICATION PLANTS

Plant Size, Million GPD	Capital Costs		
	¢/GPD Capacity		Treatment Plant Only, $
	Including Pumping Stations	Treatment Plant Only	
1	32.0	23.8	238,000
10	15.0	11.9	1,190,000
100	7.0	5.5	5,500,000

Appreciable potential capital savings could accrue in ozone-treatment plants. Two obvious areas are ozone generators and ozone contactors. In view of the vast new market that would open up if the ozonation process were to prove practical, research in new techniques of ozone generation could be justified by industry, and lowered ozone-treatment costs might be expected. The depicted contactor design, with its complexity and multiplicity of units, results in relatively high costs. Improvements in design and layout can be anticipated as ozone-treatment plants are built and operated. A capital cost estimate of the 10-million GPD plant, incorporating anticipated savings, is presented in Table XVII. The savings were estimated to be 20% on ozonation equipment, 10% on contactors, and 10% on pumps and piping. The savings amount to 11% of the total capital costs.

TABLE XVII

CAPITAL COST ESTIMATE FOR IMPROVED OZONE-TREATMENT PLANTS
OF 10-MILLION GPD CAPACITY

Cost Item	Capital Cost/Item		
	Existing Technology, $	Savings For Improved Technology, %	Improved Technology, $
1. Ozone generators	330,000	20	264,000
2. Recycle system	160,000		160,000
3. Contactor	207,000	10	186,300
4. Piping and pumps	127,000	10	114,300
5. Facilities and buildings	65,400		65,400
6. Vacuum deaeration system	7,500		7,500
Subtotal	896,900		797,500
7. Contingency and profit at 20%	179,400		159,500
8. Total	1,076,300		957,000
9. Total in round figures	1,080,000	11	957,000

OPERATING COSTS

Operating cost estimates have been divided into two parts, corresponding to plants with and without pretreatment (Tables XVIII and XIX). Included, for comparison, in the estimates of plants without pretreatment are costs for an activated-carbon treatment plant and for the ozone plant incorporating the improved technology discussed in the previous chapter. The estimates for the activated carbon treatment plant are those derived from the operation of the Pomona Pilot Plant as reported by Parkhurst et al[1].

Labor and maintenance costs for the ozone treatment plants are based on the operating experience of the Belmont Water Treatment Plant of the Philadelphia Water Department, as reported by Bean[21]. The operation of this ozone-treatment plant is very similar to the ozone-treatment plants proposed herein, and operating costs should be similar. The maintenance cost at the Belmont plant averaged $3,300 per year for a plant investment of $1,000,000. This ratio of costs to investment was maintained for six years. Operating labor costs at Belmont for the years reported averaged $7,800. These costs were adjusted to 1968 levels by use of the Maintenance Cost Index reported in the June 3rd issue of the Chemical Engineering Magazine and were used for the ozone plants of 1-and 10-million GPD. The 100-million GPD plant was assumed to require twice the labor force. Labor costs for plants with pretreatment were taken at twice those required for plants with no pretreatment.

Electrical power required for ozone generation in the improved technology plant was assumed to be 80% of that for existing methods. This resulted in an overall reduction in electrical requirements of 11.4%. Oxygen costs were calculated from industrial pricing schedules in current usage. The cost for coagulant (alum) was taken at $57.00 per ton, and for sulfuric acid at $32.00 per ton.

TABLE XVIII

OPERATING COSTS OF TERTIARY TREATMENT PLANTS WITH NO PRETREATMENT REQUIRED

Plant Capacity ——→	1-Million GPD	10-Million GPD			100-Million GPD
Type Plant ——→	Ozone	Ozone		Activated Carbon	Ozone
	Existing Technology	Existing Technology	Improved Technology	Existing Technology	Existing Technology
Capital Cost, $	202,000	1,080,000	957,000	1,670,000	7,460,000
Operating Cost, $/10^6 Gal.					
Amortization, 15 yrs. at 4%	49.60	26.50	23.50	41.00	18.31
Power (1)	36.00	28.80	25.50	8.50	21.60
Labor	25.60	2.60	2.60	15.00	0.50
Maintenance	1.80	1.00	0.90	5.00	0.67
Carbon Regeneration:					
Power, Gas, Water				2.50	
Make-up Carbon (10% Loss)				11.00	
Oxygen	24.00	17.80	17.80		8.00
Total $/10^6 Gal.	137.00	76.70	70.30	83.00	49.08
Operating Cost, ¢/10^3 Gal.	13.7	7.7	7.0	8.3	4.9

(1) Power Rates = 1¢/KWH for 1-million GPD
0.8¢/KWH for 10-million GPD
0.6¢/KWH for 100-million GPD

TABLE XIX

OPERATING COSTS OF OZONE TREATMENT PLANTS REQUIRING PRETREATMENT

Plant Capacity ——————>	1-Million GPD	10-Million GPD	100-Million GPD
Type Plant ——————>	Ozone	Ozone	Ozone
Capital Cost, $	440,000	2,270,000	12,960,000
Operating Cost, $/$10^6$ Gal.			
Amortization, 15 yrs. at 4%	108.20	55.70	31.80
Power (1)	44.50	37.30	30.10
Labor	51.20	5.20	1.00
Maintenance	4.00	2.00	1.20
Oxygen	24.00	17.80	8.00
Coagulant (Alum) (132 mg/l)	31.40	31.40	31.40
Acid (H_2SO_4) (63 mg/l)	8.40	8.40	8.40
Total $/$10^6$ Gal.	271.70	157.80	111.90
Operating Cost, ¢/10^3 Gal.	27.2	15.8	11.2

(1) Power Rates = 1¢/KWH for 1-million GPD,
0.8¢/KWH for 10-million GPD
0.6¢/KWH for 100-million GPD

REFERENCES

1. Parkhurst, J.D., Dryden,F.D., McDermott, G.N., English, J., "Pomona Activated Carbon Pilot Plant", J. Water Polution Control Fed., 39 (2), R70-81 (1967).

2. Morris, J.C., Weber, W.J.,Jr., Adsorption of Biochemically Resistant Materials from Solution-2, 999-WP-33, AWTR-16, pp 93-94, Federal Water Pollution Control Administration, Cincinnati, O., 1966.

3. Smith, F.E., "Ozone Applications", Report No. I.G.E. 150, Airco, Industrial Gases Div., Jersey City, N.J., Apr. 18, 1967.

4. Toricelli, A., "Drinking Water Purification", Ozone Chemistry and Technology, p 453, American Chemical Society, Washington, D.C., March, 1959.

5. American Public Health Association, Standard Methods for the Examination of Water and Wastewater, Twelfth Edition 1963-66, p 366, APHA, New York, 1966.

6. Ibid, pp 510-514.

7. Ibid, p 193.

8. Kilpatrick, Mary L., Herrick, C.C., and Kilpatrick, Martin, "The Decomposition of Ozone in Aqueous Solution", J. American Chemical Society, 78, 1784 (1956).

9. Bailey, K.C., Retardation of Chemical Reactions, p 295, Longmans Green, New York, 1937.

10. Kassel, L.S., Kinetics of Homogeneous Gas Reactions, p 264, Chemical Catalog Co., New York, 1932.

11. Yost, D.M., Russell, H., Systematic Inorganic Chemistry, p 265, Prentice-Hall, New York, 1944.

12. Leva, M., Tower Packings and Packed Tower Design, Second Edition, The United States Stoneware Company, 1953.

13. Koppe, P., Giebler, G., "Ozone Decomposition in Water", Gass Wasserfach, 107(8), 196-200 (1966); Chemical Abstracts, 65, 489 d (1966).

14. The Welsbach Corporation, Philadelphia, Pa., Bulletin 201, May 1965.

15. Cromwell, W.E., Manley, T.C., "Effect of Gaseous Diluents on Energy Yield of Ozone Generation from Oxygen", Ozone Chemistry and Technology, p 304, American Chemical Society, Washington, D.C., March, 1959.

16. Inoue, E., Sugino, K., "Inhibiting Action of Hydrocarbons on Ozone Formation by Silent Electrical Discharge", Ozone Chemistry and Technology, p 313, American Chemical Society, Washington, D.C., March, 1959.

17. Guinvarc'h, Pierre, "Three Years of Ozone Sterilization of Water in Paris", Ozone Chemistry and Technology, p 416, American Chemical Society, Washington, D.C., March, 1959.

18. Koenig, Louis, "The Cost of Water Treatment by Coagulation, Sedimentation, and Rapid Sand Filtration", J. Am. Water Works Assoc., 59, 290-336 (1967).

19. Bishop, D.F., Marshall, L.S., O'Farrell, T.P., Dean, R.B., "Activated Carbon for Waste Water Renovation: II. Removal of Organic Materials by Clarification and Column Treatment", Paper presented at 149th National Meeting of the American Chemical Society, April 6, 1965, Detroit, Michigan.

20. Slechta, A.F., Culp, G.L., "Water Reclamation Studies at the South Tahoe Public Utility District", J. Water Pollution Control Fed., 39 (5), 787 (May 1967).

21. Bean, E.L., "Ozone Production and Costs", Ozone Chemistry and Technology, p 430, American Chemical Society, Washington, D.C., March, 1959